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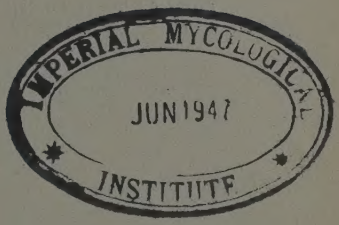

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MATHÉMATIQUES

PROLONGEMENT ANALYTIQUE ET ULTRACONVERGENCE

Par A. MARKOUCHEVITCH

(Présenté par S. N. Bernstein, de l'Académie, le 21.I.1944)

1. Théorème I. *Il existe une suite de nombres complexes* $\{\theta_j\}$* $(\overline{\lim_{j\to\infty}} \sqrt[j]{|\theta_j|} = \overline{\lim_{j\to\infty}} \sqrt[j]{|1-\theta_j|} = 1)$ *et deux suites croissantes d'entiers positifs* $\{n_k\}$ *et* $\{m_k\}$ *telles que pour chaque fonction* $f(z)$, *analytique à l'origine de coordonnées, on a le développement*

$$f(z) = \lim_{k\to\infty} \sum_{j=0}^{n_k} \theta_j \frac{f^{(j)}(0)}{j!} z^j + \lim_{k\to\infty} \sum_{j=0}^{m_k} (1-\theta_j) \frac{f^{(j)}(0)}{j!} z^j \qquad (1)$$

*qui converge uniformément «à l'intérieur»*** *de l'étoile rectiligne de Mittag-Leffler de la fonction* $f(z)$.

Démonstration. Considérons la fonction $\frac{1}{1-z}$ dans son étoile S. Les fonctions $\{z^n\}$ forment, comme il est facile à voir, un système de fonctions fortement, linéairement indépendantes ([1],[2]) dans l'espace des fonctions analytiques en S, et, par conséquent ([1],[2]), le développement formel de $\frac{1}{1-z}$ suivant les puissances de z

$$\frac{1}{1-z} \sim 1 + z + z^2 + \dots$$

peut être décomposé en une somme de deux développements

$$\varphi(z) \sim \theta_0 + \theta_1 z + \theta_2 z^2 + \dots$$
$$\psi(z) \sim (1-\theta_0) + (1-\theta_1) z + (1-\theta_2) z^2 + \dots$$

dont chacun possède une suite partielle de sommes partielles qui converge uniformément «à l'intérieur» de S vers $\varphi(z)$ et $\psi(z)$, respectivement:

$$\varphi(z) = \lim_{k\to\infty} \sum_{0}^{n_k} \theta_j z^j, \qquad \psi(z) = \lim_{k\to\infty} \sum_{0}^{m_k} (1-\theta_j) z^j$$

Soit maintenant S_f l'étoile de $f(z)$ et γ un contour fermé de Jordan rectifiable, étoilé par rapport à l'origine et d'ailleurs arbitraire. Alors pour chaque z intérieur à γ on a

* Les nombres $\{\theta_j\}$ peuvent être supposés réels.
** C'est-à-dire sur chaque ensemble fermé de points de l'étoile.

$$f(z)=\frac{1}{2\pi i}\int_\gamma \frac{f(\zeta)}{\zeta}\frac{d\zeta}{1-\frac{z}{\zeta}}=\frac{1}{2\pi i}\int_\gamma \frac{f(\zeta)}{\zeta}\varphi\left(\frac{z}{\zeta}\right)d\zeta+\frac{1}{2\pi i}\int_\gamma \frac{f(\zeta)}{\zeta}\psi\left(\frac{z}{\zeta}\right)d\zeta=$$

$$=\lim_{k\to\infty}\sum_0^{n_k}\theta_j z^j\frac{1}{2\pi i}\int_\gamma \frac{f(\zeta)}{\zeta^{j+1}}d\zeta+\lim_{k\to\infty}\sum_0^{m_k}(1-\theta_j)z^j\frac{1}{2\pi i}\int_\gamma \frac{f(\zeta)}{\zeta^{j+1}}d\zeta=$$

$$=\lim_{k\to\infty}\sum_0^{n_k}\theta_j\frac{f^{(j)}(0)}{j!}z^j+\lim_{k\to\infty}\sum_0^{m_k}(1-\theta_j)\frac{f^{(j)}(0)}{j!}z^j$$

ce qu'il fallait démontrer.

2. Comme exemple, considérons les valeurs suivantes de $\{n_k\}$, $\{m_k\}$, $\{\theta_j\}$:

$$n_k=[e^{(2k+2)^p}],\quad m_k=[e^{(2k+1)^p}],$$

p étant un nombre réel supérieur à 1 et d'ailleurs arbitraire*, $\theta_0=1$

$$\theta_j=\sum_{k=0}^{\infty}\left\{\sum_{n=j}^{n_k}\frac{j!}{n!}\alpha_{n_k}^j\beta_{n_k}^n E_n^j-\sum_{n=j}^{m_k}\frac{j!}{n!}\alpha_{m_k}^j\beta_{m_k}^n E_n^j\right\}\qquad (j>0)$$

où $\alpha_{nk}=\frac{2}{\ln(2k+2)}$, $\beta_{nk}=1-\sqrt{\frac{1}{2k+2}}$ et E_n^j sont les coefficients des polynômes suivants:

$$z(1+z)\ldots(n-1+z)=E_n^1 z+E_n^2 z^2+\ldots+E_n^n z^n\quad (n=1,\ 2,\ \ldots)$$

Les suites indiquées s'obtiennent suivant les principes exposés dans la Note précédemment citée (2) au moyen du développement un peu modifié de Fredholm (3) pour la fonction $\frac{1}{1-z}$.

3. Le théorème précédent donne une méthode pour effectuer le prolongement analytique; cette méthode se rattache aux méthodes classiques de Mittag-Leffler, Painlevé et Borel. Ce qu'il y a de nouveau s'obtient au moyen du principe élémentaire de décomposition précédemment exposé dans les Notes (1,2). Remarquons que le théorème I reste valable pour le prolongement dans les étoiles curvilignes (les constantes $\{\theta_j\}$, $\{n_k\}$, $\{m_k\}$ dépendent du type de l'étoile).

4. Le théorème I conduit à la décomposition de la série potentielle pour la fonction $f(z)$ en une somme de deux séries ultraconvergentes dans l'étoile de $f(z)$ (en ce qui concerne la ultraconvergence des séries potentielles en général, voir, par exemple, (4)). En s'appuyant sur les résultats que nous avons exposés dans (1) et (2), on peut énoncer un théorème plus général, mais, en même temps, un peu plus faible.

Théorème II. *Si G est un domaine arbitraire simplement connexe contenant l'origine et $f(z)$ une fonction analytique dans G. la série* $\sum_0^{\infty}\frac{f^n(0)}{n!}z^n$ *est ou bien ultraconvergente en G (c'est-à-dire contient une suite partielle de sommes partielles qui converge uniformément vers $f(z)$ «à l'intérieur» de G), ou bien elle peut être décomposée en une somme de deux séries potentielles* $\sum_0^{\infty}\theta_n\frac{f^n(0)}{n!}z^n$ *et* $\sum_0^{\infty}(1-\theta_n)\frac{f^n(0)}{n!}z^n$ *ultraconvergentes en G (les nombres $\{\theta_n\}$ dépendent, en général, de G; et de $f(z)$).*

5. D'autre part, le théorème II peut être étendu à une classe plus vaste de séries de fonctions analytiques. Indiquons, par exemple, la proposition suivante:

* Il ne peut pas être remplacé par un nombre inférieur à 1.

Théorème III. *Si* $\{f_n(z)\}$ *est une suite de fonctions analytiques en* G *qui présente une base pour l'espace de fonctions analytiques en un certain domaine* g *contenu dans* G *(c'est-à-dire telle que chaque fonction analytique en* g *peut être développée d'une manière unique en une série en* $\{f_n(z)\}$ *convergeant uniformément «à l'intérieur» de* g*), alors pour chaque fonction* $f(z)$ *analytique en* G *son développement formel* $f(z) \sim \sum_0^\infty a_n f_n(z)$ *(le seul développement suivant les fonctions* $\{f_n(z)\}$ *qui converge vers* $f(z)$ *en* g*) est ou bien ultraconvergent dans* G*, ou bien il peut être décomposé en une somme de deux développements* $\sum_0^\infty \vartheta_n a_n f_n(z)$ *et* $\sum_0^\infty (1-\vartheta_n) a_n f_n(z)$ *ultraconvergents en* G *(les nombres* $\{\vartheta_n\}$ *dépendent, en général, de* G*,* $\{f_n(z)\}$ *et* $f(z)$*).*

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MECHANICS

ON LARGE DEFLECTIONS OF CORRUGATED MEMBRANES

By D. J. PANOV

(Communicated by S. A. Khristianovich, Member of the Academy, 7.IV.1944)

1. An earlier paper (1) by the author has been concerned with large deflections of a round slightly corrugated membrane. Proceeding from the general equations of the theory of shells as developed by Love in his well-known book (2), the author has obtained the following expressions:

$$\left.\begin{aligned} &\frac{2Eh^3}{3(1-\sigma^2)}\left(r\frac{d^3w}{dr^3}+\frac{d^2w}{dr^2}-\frac{1}{r}\frac{dw}{dr}\right)-2Eh\frac{dw}{dr}\psi-2kEh\frac{df}{dr}\psi-Z=0\ *\\ &r\frac{d^2\psi}{dr^2}+\frac{d\psi}{dr}-\frac{1}{r}\psi+\frac{1}{2}\left(\frac{dw}{dr}\right)^2+k\frac{dw}{dr}\frac{df}{dr}=0\end{aligned}\right\} \qquad (1)$$

They present approximate equilibrium equations for a shell of revolution, slightly curved and symmetrically loaded, which has its meridian expressed by the equation

$$z=kf(r) \qquad (2)$$

In these equations w is the strain component directed along the normal to the middle surface of the shell; h is a half of the shell's thickness; ψ is a function of stresses determined by the equation $2Eh\psi=rT_1$; Z is a function of a load applied normally to the middle surface; the parameter k is supposed to be small enough. The system (1) is a direct generalization of Karman's system of equations of large deflections of a plate, written in the form given to it by Prescott (3), which it assumes for $k=0$. In (1) an approximate solution of system (1) was obtained. It is accurate up to the third power of the load parameter and to the first power of the parameter k. By means of it one of the phenomena observed to take place on the deformation of corrugated membranes under pressure has been explained, but, on the other hand, it has failed to account for several other phenomena characterized by those terms of the solution which depend upon a certain power of the parameter k. In this respect the solution had to be refined, and it was refined. The result of this work is reported below.

2. Considering the problem of deformations under hydrostatic load of a slightly corrugated membrane, we put in equations (1)

$$Z=\frac{1}{2}pr^2$$

where p is the intensity of the hydrostatic load, and

$$f(r)=\sin\frac{1-\rho}{\Omega}$$

where $\rho=r/R$, $\Omega=2/\pi(2n+1)$ and determines the corrugation wave frequency.

* In (1) the first equation of the system (1) contained, moreover, a term of order h^2/R^2. This term is here omitted on account of its smallness in comparison with the other terms.

The solution of equations (1) is subject to the boundary conditions

$$w(R) = w'(R) = w'(0) = 0$$
$$\psi(0) = 0;\ R\psi'(R) - \sigma\psi(R) = 0$$

characterizing a membrane rigidly held along the contour. Putting

$$\frac{dw}{dr} = \sum\sum \theta_{ij} p^i k^j;\quad \psi = \sum\sum \psi_{ij} p^i k^j \tag{3}$$

we find in succession

$$\theta_{10} = A_{10}(\rho^3 - \rho) \qquad A_{10} = \frac{3(1-\sigma^2)R^3}{32Eh^3}$$
$$\theta_{20} = 0$$
$$\theta_{30} = A_{30}\left(2\rho^{11} - 15\rho^9 + 50\rho^7 - \frac{110-90\sigma}{1-\sigma}\rho^5 + \frac{150-90\sigma}{1-\sigma}\rho^3 - \frac{77-37\sigma}{1-\sigma}\rho\right)$$
$$A_{30} = -\frac{9(1-\sigma^2)^4 R^{11}}{80\cdot 32^4 \cdot E^3 h^{11}}$$
$$\theta_{11} = 0$$
$$\theta_{21} = A_{21}\left[\frac{1}{1-\sigma}(8\rho^5 - 24\rho^3 + 18\rho) + \left(\rho^3 - 4\rho^4 + 6\rho^2 - \frac{5-3\sigma}{1-\sigma}\right)\cos\frac{1-\rho}{\Omega}\right] + O(\Omega^3)$$
$$A_{21} = -\frac{9(1-\sigma^2)^3 R^8}{32^3 E^2 h^6}\Omega$$
$$\theta_{31} = 0$$
$$\theta_{12} = A_{12}\left(\frac{1}{4}\rho\ln\rho - \frac{1}{16}\rho^3 + \frac{1}{16}\rho + \frac{3}{4}\rho\,\mathrm{Ci}\,\frac{2\rho}{\Omega} - \frac{3}{4}\rho\,\mathrm{Ci}\,\frac{2}{\Omega} - \frac{\Omega}{4}\sin\frac{2\rho}{\Omega}\right) + O(\Omega^2)$$
$$A_{12} = -\frac{9(1-\sigma^2)^2 R^5}{32Eh^5}$$
$$\theta_{22} = 0$$
$$\cdots\cdots$$
$$\psi_{10} = 0$$
$$\psi_{20} = B_{20}\left(\rho^7 - 4\rho^5 + 6\rho^3 - \frac{5-3\sigma}{1-\sigma}\rho\right) \qquad B_{20} = -\frac{3(1-\sigma^2)^2 R^7}{32^3 E^2 h^6}$$
$$\psi_{30} = 0$$
$$\psi_{11} = B_{11}\left[(1-\rho^2)\cos\frac{1-\rho}{\Omega} - \frac{2}{1-\sigma}\rho\right] + O(\Omega^3) \qquad B_{11} = \frac{3(1-\sigma^2)R^4}{32Eh^3}\Omega$$
$$\psi_{21} = 0$$
$$\cdots\cdots$$

It was taken into account in computing the expressions (3) that the ordinary case in practice was $n \geqslant 7$, *i. e.* $\Omega < 0.043$, $\Omega^2 < 0.002$ and therefore terms of the order Ω^2 and higher (compared to the main terms) were discarded.

Once an approximate expression for dw/dr is found, it is easy to find w and determine the maximum deflection of the membrane $W = w(0)$. Introducing a dimensionless parameter

$$\nu = \frac{(1-\sigma^2)R^4}{Eh^4}p$$

we have

$$\frac{W}{h} = \frac{3}{128}\left[1 - \frac{9}{16}(1-\sigma^2)\left(\frac{a}{h}\right)^2\right]\nu +$$
$$+\left(\frac{3}{128}\right)^2\left[\frac{5(1+\sigma)}{3}\Omega\frac{a}{h}\right]\nu^2 - \left(\frac{3}{128}\right)^3\left[\frac{1+\sigma}{1440}(173-73\sigma)\right]\nu^3$$

Here a is the corrugation wave amplitude, connected with the parameter k by the relation $a = kR$.

3. In order to reduce the formula (5) to a form analogous to Griffith's formula (4), one has to carry out the transformations mentioned in (5). Putting

$$W=\sum\sum a_{ij}v^i a^j; \quad v=\sum\sum c_{ij}W^i a^j$$

and using the relations $c_{10}=1/a_{10}$; $c_{12}=-a_{12}/a_{10}^2$; $c_{21}=-a_{21}/a_{10}^2$; $c_{20}=-a_{20}/a_{10}^2$, we find:

$$v=\frac{128}{3}\left\{\left[1+\frac{9}{16}(1-\sigma^2)\left(\frac{a}{h}\right)^2\right]\frac{W}{h}-\frac{5}{3}(1+\sigma)\,\Omega\,\frac{a}{h}\left(\frac{W}{h}\right)^2+\right.$$
$$\left.+\frac{1+\sigma}{1440}(173-73\sigma)\left(\frac{W}{h}\right)^3\right\}$$

Introducing the membrane's thickness $\delta=2h$ and the corrugation depth $H=2a$, we can write

$$p=\frac{16E\delta^4}{3(1-\sigma^2)R^4}\left\{\left[1+\frac{9}{16}(1-\sigma^2)\left(\frac{H}{\delta}\right)^2\right]\frac{W}{\delta}-\frac{10}{3}(1+\sigma)\,\Omega\,\frac{H}{\delta}\left(\frac{W}{\delta}\right)^2+\right.$$
$$\left.+\frac{1+\sigma}{360}(173-73\sigma)\left(\frac{W}{\delta}\right)^3\right\}$$

This formula is an immediate generalization of Griffith's formula, whose extension to the case of corrugated membranes it presents and into which it passes for $H=0$.

4. By computing the subsequent terms in the expansions (3), the solution is refined further still.

The system of equations (1) affords also the possibility of solving a number of problems on large deflections of symmetrical shells of revolution of different shape determined by the function $f(r)$.

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ASTRONOMY

A METEORIC THEORY OF THE ORIGIN OF THE EARTH AND PLANETS

By O. J. SCHMIDT, Member of the Academy

1. For the present there is no generally recognized theory of the origin of the Earth and planets. All former theories have been found to be irreconcilable with facts. And in working out a new theory one has to work it out from the new facts that have become known to astronomers within these two decades and been not yet turned to full account in cosmogony.

Two of these facts, the rotation of the Galaxy and the presence near its central plane of big masses of obscuring matter (dust-like and meteoric); lie at the basis of the theory put forward in the present paper. This theory rests on the following conception: the Sun on its galactic course once crossed a dark cloud (of dust and meteorites) and; having entrained part of its matter; compelled the captured particles to revolve about it as a centre. Eventually these particles united into large formations—the planets.

The purpose of the theory is to put this conception into the language of equations and formulae; and upon deriving some quantitative conclusions check them against the known data of observation.

In the face of G a l a c t i c R o t a t i o n, which has since 1926 been a definitely established fact, it is no longer possible to support the simplified schemes (models) which heretofore were placed at the basis of the theory of stellar motion. It will not do to-day either to compare the stars to gas molecules or reduce the problem to a case of interaction between two (or three) isolated objects. Two stars while performing their complicated motions in the Galaxy; — which are each a combined result of attraction by the central galactic masses and of the actions of external masses and the neighbouring individual stars — can happen to come in a position where the external forces tend to draw them so closely together that capture and formation of a double star takes place.

In an earlier paper (1) the author has advanced a theory in which the formation of visual binary stars is supposed to occur by such a capture under conditions of a rotating Galaxy. In it have been adopted the following simplifying assumptions considered as typical; *i. e.* corresponding to statistical average:

a) The stars move along circular orbits being subject to attraction by the mass of the Galaxy which is conceived to be concentrated in the centre.

b) The orbits lie in different planes forming small but significant angles between each other.

c) The exact instant at which capture takes place is when the two stars pass the position of the shortest distance between the orbits.

On these assumptions the formula

$$\frac{1}{1 \mp e} - \frac{1}{2} = \frac{a}{p} \qquad (1)$$

has been derived (1); where e and a are the eccentricity and the semi-major axis of the new formed double star's orbit; respectively, and the quantity p does not

depend upon the elements of the relative orbit; but solely upon the galactic parameters of the stars; namely:

$$\rho = R\frac{M}{\mathrm{M}}\frac{1}{2\sin^2\frac{\alpha}{2}} \qquad (2)$$

Here R is the distance to the centre of the Galaxy; M is the total mass of the two stars; M is the mass of the inner part of the Galaxy: α is the angle between the orbital planes of the stars previous to capture. The quantity ρ is the limiting value of the capture distance d; above which no capture is possible. If $d > \rho/_2$, then e in formumula (1) is to be taken with the upper sign; while the lower sign corresponds to $d < \rho/_2$. With $d = \rho/_2$ the orbit is a circumference.

Formula (1) has provided a simple explanation of all the principal laws established by the statistics of visual binaries; and; moreover; there has proved to be a remarkable numerical agreement between theory and observation.

The above-stated simplifying assumptions (circular orbits; *etc.*) are not, of course; as a general case exactly fulfilled in nature. Therefore formula (1) is an approximate relation and is only true in the m e a n for a large number of objects.

This formula and the same concept of capture will now be used in analysing the capture of meteoric matter by a solitary star; the Sun.

2. The interstellar and interplanetary matter comes up in different cosmogonic theories of which the most recent are those by B. Lindblad (2) and H. Alfvén (3). According to the author's theory, planets arise from interstellar matter captured by the Sun in its galactic motion.

Essential to this theory is the fact that the plane of the Sun's galactic orbit is inclined at a certain angle (of about 3°) to the central plane of the Galaxy. If the Sun while at one of the nodes of its orbit passes through a cloud of matter (meteorites; dust); meteorites are captured according to the same laws as underlie the formation of double stars. A meteorite thus captured moves about the Sun along Kepler's orbit. As has been explained in the cited paper on double stars, the plane of the relative motion of the binary system is determined by the direction of the two following straight lines: the shortest distance between the original orbits, and the relative velocity of the two stars previous to capture. Supposing; in accordance with the latest data; that the meteoric cloud is all nearly in one plane (the central plane of the Galaxy); the captured meteorites will move in a swarm also nearly in one plane; thus forming a flat lens. The characteristic of their orbits is given by formula (1) which for simplicity we can use with the upper sign only; giving e values ranging from —1 to +1. Within these limits all values of e are equiprobable, as has been shown in the above-mentioned paper. To be sure; all meteorites are not exactly in the position of the shortest distance between the original orbits when their capture takes place. Some are captured when they have already passed this position; and others again when they have not yet reached it. This goes somewhat to increase the difference between the planes of the new orbits; so that a slightly thicker lens is formed, and we may be certain to meet with statistical deviations from formula (1).

The initial velocity of the relative motion is the relative velocity of the meteorite at the instant of capture. As the position of the meteorite at that moment can as well be to one side of the Sun as to the other; both direct and inverse motions will arise. The odds in favour of either direction would be equal if only the cloud was one of perfectly uniform density. If, however; the density of the cloud in the region crossed by the Sun is not uniform (say; the Sun passes near the edge of the cloud); then more meteorites are captured on one side than on the other. Accordingly, by far the larger number of meteorites forms a swarm revolving about the Sun in one direction only. The rest revolve in the opposite sense and these are bound to collide sooner or later with some portion of the main swarm. The colliding meteorites lose their rotational momentum and fall on the Sun.

3. Within the swarm; the forces of interaction between the individual meteorites come into play. An exchange of energy and momentum takes place (while the

total energy and amount of rotation remain invariable), which again results in some of the meteorites falling on to the Sun. But the main mass segregates by and by into larger bodies and this is the formation of planets. What we observe at this date as separate meteorites is the remainder of this process. The segregation of the meteoric swarm proceeds through smaller particles falling upon the larger ones in she same way as we know meteorites and meteors to fall on the Earth. As the orbits of the meteorites do not differ greatly from one another, the relative velocities are rather small, and the impact caused by the fall must not, as a rule, lead to volatilization or scattering in every direction, which contingency has been often used as an argument against various meteoric hypotheses. This point has been cleared up in Lindblad's paper ([3]).

We speak of meteorites and of dust as two distinct phenomena, but the difference is merely in size rather than principle. Dust clouds are likely to include larger particles upon which dust particles settle. In a meteoric swarm formed about the Sun this process of condensation must go on at a higher rate because of the greater density of the swarm as compared to that of a dust cloud. In the case of dust particles and small meteorites the effect of light pressure needs to be inquired into. It is known ([5],[6]) that a particle of small; but finite, size revolving adout the Sun is losing momentum under the influence of light pressure and in the long run, if isolated; will fall on the Sun. But ours are not isolated particles; and; therefore; only a small number of them will settle down on the Sun. The rest; by dint of continuous interaction; will have this loss of momentum distributed among themselves; and most of them, moreover, will rather soon be united into larger bodies, thus giving rise to planets. So the pressure of light makes only for a more thorough intermixing of meteorites; thereby accelerating slightly the formation of planets, but does not in the least affect the ultimate outcome.

4. What can we conceive to be the main features of a planetary system formed according to this scheme?

As the swarm of meteorites has the form of a flat lens, the planets in progress of formation have their orbits lying approximately in one plane which is the central plane of the lens. As the meteorites are revolving mainly in one direction, the planets will be revolving in this one direction also.

The meteorites of the swarm move along ellipses for which the distribution of eccentriticies and axes is given by formula (1). At the beginning the major axes have a dominant direction (along the shortest distance between the galactic orbits of the Sun and the cloud); but are soon deflected from it owing to reciprocal perturbation in all directions. For that reason no planet arising from an aggregate of a very large number of meteorites can have a preferential direction in which its orbit would be elongated. Only a circular orbit; or nearly so; is possible in this case.

Thus, what we know to be the main features of our planetary system follows directly from the suggested theory.

The angular momenta of the planets; which were the stumbling block of the former theories, are obtained on this theory directly from the galactic momentum of meteorites.

The further development of the theory will bring within its compass such problems as the rotation of the Sun; the rotation of planets; the formation of satellites, the age of the planetary system.

Certain features of the internal structure of the Earth can also be derived from this theory. Some of these problems are discussed in the papers that are now being prepared for the press. The present communication will only give the first quantitative results.

5. From formula (1) may be derived some consequences concerning the distribution of mass and momentum in the planetary system. Suppose for simplicity sake that the portion of the meteoric mass fallen to the Sun can be neglected.

Theorem I. *The total momentum of the system is equal to that of a single planet supposed to have a mass equal to the total mass of the planets revolving in a circular orbit at a distance* $\rho/2$ *from the Sun.*

As has been mentioned above, all values of e between -1 and $+1$ are equiprobable, the total mass of the meteorites m is distributed evenly over these values, and, the range of e equalling 2, we have $dm = \frac{m}{2} de$. The momentum of a particle with a mass dm, eccentricity e and semi-axis a is $k\sqrt{M}\sqrt{a(1-e^2)}\,dm$, where k^2 is the gravitation constant, M is the mass of the Sun. As it follows from (1) that

$$a(1-e^2) = \frac{\rho}{2}(1+e)^2$$

we obtain for the momentum the expression

$$k\sqrt{M}\sqrt{\frac{\rho}{2}(1+e)}\,dm = k\sqrt{M}\sqrt{\frac{\rho}{2}}\,\frac{m}{2}(1+e)\,de \qquad (3)$$

Integration over e from -1 to $+1$ gives the total momentum of the system

$$k\sqrt{M}\sqrt{\frac{\rho}{2}}\,m$$

and this establishes Theorem I.

Let us further consider the problem of the boundary of the solar system. Believing the planets to have been formed from meteorites, part of which still continues in a free state, is obviously incompatible with the idea of the planetary system having a strict boundary. Individual meteorites can deviate from formula (1) which is only true in the mean, and there is no limit therefore to the distance at which some particular meteorites may be supposed to perform their revolutions about the Sun. Yet the main mass of meteorites obey formula (1), and their momentum cannot possibly exceed the maximum which this formula admits. This maximum momentum corresponds to $e = +1$. Substituting this value in formula (3), we obtain

$$k\sqrt{M}\sqrt{\frac{\rho}{2}}\,2dm = k\sqrt{M}\sqrt{2\rho}\,dm$$

which gives the momentum on a circular orbit of radius 2ρ. Taking now for the «practical boundary» of the solar system the distance beyond which the existence of but quite an insignificant portion of the total planetary mass is possible, we can establish the following theorems:

Theorem II. *The practical boundary of the planetary system runs at a distance of* 2ρ *from the Sun.*

Theorem III. *The practical boundary of the planetary system is as far a way from the Sun as four times the radius of the circular orbit which a planet, having the total mass and momentum of all planets taken together, may be imagined to describe about the Sun.*

This theorem is an immediate consequence of Theorems I and II and is remarkable for not involving the quantity ρ.

6. Though the motion of the Sun is no circular one, and neither formulae (1) and (2) nor the theorems deduced from them can possibly apply to it accurately, they yet are useful as a first approximation in describing the structure of our planetary system and verifying how far the results obtained agree with the observational values.

If the distance from the Earth to the Sun, the orbital momentum of the Earth and the mass be put at unity, then the total mass of the planets is known to be 446, and the total momentum, 1176 (cf. [7]; Table 1). The ratio of total momentum to total mass is 2.64. For the imaginary «total» planet to have this momentum—mass ratio it must be supposed to revolve at a distance of 2.64^2 from the Sun, which is 7 astronomical

units. The practical boundary of the solar system lies near the orbit of Neptune, that is, about 30 astronomical units away from the Sun. Dividing 30 by 7 we get 4.3 instead of 4, which is the figure required by Theorem III. The agreement is satisfactory.

A distance of 7 astronomical units corresponds, according to Theorem I, to $\rho/2 = 7$ or $\rho = 14$. Now, what is the value of ρ obtained directly from formula (2)? It depends upon how far from the centre of the Galaxy the capture of meteorites by the Sun took place. The present distance of the Sun from the centre of the Galaxy is estimated by the majority of workers as about 7500 parsecs. An osculating orbit of the Sun ([4]) gives a maximum distance of 14200 parsecs. Assume; moreover; that the internal mass of the Galaxy is 10^{11} times the mass of the Sun and that the orbit of the Sun is inclined at an angle $\alpha = 3°$. Then formula (2) gives the following limits of the variation of ρ as a function of R (in astronomical units):

$$11.3 < \rho < 21.4$$

Within these limits lies also the value of $\rho = 14$ which we have obtained before.

Thus, our formulae, though of approximate nature and based on simplifying assumptions, prove to yield such quantitative estimates as come close to the observed data.

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Correction

In the article by O. J. Schmidt, C. R. Acad. Sci. URSS, XLIV, No. 1, page 10, line 3 from the top

instead of $\rho = R\frac{M}{M}\frac{1}{2\sin^2\frac{\alpha}{2}}$, read $\rho = R\frac{M}{M}\frac{1}{2\sin^2\frac{\alpha}{2}}$.

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GEOPHYSICS

THE CONTINENTAL EFFECT IN THE GEOGRAPHIC DISTRIBUTION OF THE ELECTRON CONCENTRATION IN THE F_2-LAYER

By V. N. KESSENIKH and N. D. BULATOV

(Communicated by N. D. Papalexi, Member of the Academy, 19.IV.1944)

The existing method of forecasting the limiting frequencies employed for communication by radio-waves reflected by the ionosphere depends upon making use of the graphs of the daily course of the critical frequencies (or; correspondingly, the electron concentration) for various latitudes and plotting the ionization charts on the basis of these graphs. It is known that in the first approximation this method has shown its worth; since the factor determining the ionization—the solar energy emerging in the atmosphere—is independent of the state of the Earth's surface; and the geographic distribution of the intensity of radiation periodically changes according to the same law for all points at the same latitude with a phase shift corresponding to the difference in longitude.

It is on this circumstance that the idea of employing mobile ionization charts is based [1,2].

However, the F_2-layer possesses well-known peculiarities in the daily and seasonal course of ionization, which until now were not satisfactorily explained and should be taken into account in employing the method of ionization charts.

It is known that the maximum electron concentration in the F_2-layer is established not in the months with the maximum value of $\cos\chi$ (χ is the zenith distance to the Sun), but in the winter half of the year. An attempt to explain this seasonal course of ionization in the F_2-layer was made by Appleton and Naismith [3] by assuming that the seasonal changes in temperature of the upper layers of the atmosphere influence the electron concentration.

As is known; the development of this concept leads to the assumption of quite high gaseous temperatures; of the order of 1000° K, in the F_2-layer; and still higher electron temperatures [4].

Without entering into a discussion on the nature of the seasonal changes in the electron concentration in the F -layer; one must acknowledge the following firmly established facts:

1. The average value of daily maxima of the electron concentration in the F_2-layer during the winter half of the year is higher than its average value during the summer half.

This holds true both for the northern and southern hemispheres, though the seasonal difference for the latter is less pronounced.

2. The increase in the average values of daily maxima of the electron concentration in the F_2-layer corresponds to the seasonal fall in the average temperature and rise in pressure in the troposphere. One is not permitted to assume that there is a direct causal relation between the seasonal changes in temperature; pressure and electron concentration.

The possible considerations on the distribution of density and temperature with altitude are as yet too speculative in character to employ them to explain observed phenomena.

The corresponding changes in the theory of the distribution of the electron concentration with altitude are still the subject of manysided investigation; and their correlation with data of observations may so far be used only to choose the basic assumptions of the theory.

In spite of this incompleteness of the theory, the peculiarities in the seasonal course of the electron concentration in the F_2-layer pointed out above may be regarded as regularly connected with the thermodynamics and aerodynamics of the atmosphere, and manifestation of these same regularities should be sought for not only in the seasonal change in the electron concentration; but in its geographic distribution as well.

Already in 1935 Martyn and Pulley (4) established the indicants of the correlation between the barometric pressure at the ground level and the critical frequency of the F_2-layer. However; the data at our disposal from comparison studies of the barometric pressure and critical frequencies of the F_2-layer, generally speaking; do not give grounds for affirming the existence of a single-valued correlation between the unsmoothed course of the pressure and the electron concentration in the F_2-layer. This correlation appears only in the comparison of mean values; *i. e.* with respect to climate but not to weather. More definite data on the correlation between meteorological processes and the critical frequencies of the F_2-layer were obtained by Bannon, Higgs; Martyn and Munro (5) during an analysis of synoptic charts of meteorological data in the region where the critical frequencies were measured (Australia). On comparing the critical frequencies for the days when the frontal zones, *i. e.* zones of rapid change of the characteristics of the air in the troposphere, passed through the region of observation; with the values for the days when there were no frontal zones, the above-mentioned authors found that in the «non-frontal» days the critical frequencies in 72 per cent of the cases are higher than the values of the critical frequencies in the «frontal» days.

These data also speak in favour of the assertion as to the existence of a correlation between the changes in the state of the atmosphere over considerable regions and the electron concentration of the F_2-layer.

A comparison made of the data on the change in the critical frequency of the F_2-layer that have been obtained in Tomsk since 1936; with the data obtained in other ionospheric stations and with the climatic characteristics of these stations gives grounds for asserting that the seasonal effect in the change of the electron concentration of the F_2-layer appearing with time is connected with a similar effect of the climatic conditions in the geographic distribution of the electron concentration in the F_2-layer.

For the conditions in the central part of Asia this effect assumes such a markedly pronounced form due to the continental climate of Siberia, that one may speak of the existence of a continental effect in the geographic distribution of the electron concentration in the F_2-layer, which is of the same nature as the seasonal effect.

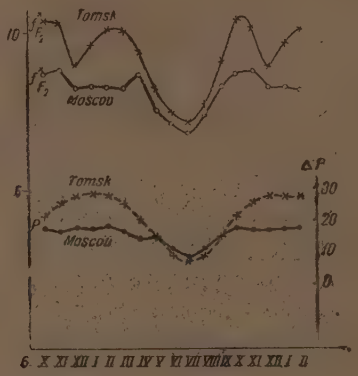
The first indications of the existence of a continental effect were obtained by us in 1938 when we compared the critical frequencies for March 1938 in Tomsk and Washington (see (3), Fig. 8).

The maximum value in Tomsk, according to the average daily curve for March 1938, was 13.7 mHz, while the corresponding value for Washington was 11.8 mHz. This fact that the critical frequency in Tomsk is higher than in Washington seemed inexplainable, since Tomsk is at a considerably higher latitude (56°28′ N) than Washington (39° N), and according to generally accepted ionization charts one should have expected that the critical frequency in Tomsk should be smaller than in Washington in the ratio of 1 : 1.07.

Observations of the ionization of the upper atmosphere begun in Moscow in 1940 have yielded data which are of especial interest when compared with the

data of the Tomsk ionospheric station, since Tomsk and Moscow differ in latitudes only by 30′, while the climatic conditions of the European part of the USSR and Siberia are strikingly different,

In the figure there is presented the course of the mean monthly values of the critical frequencies in the F_2-layer for noon-time averaged for 2 years for Tomsk and Moscow, and for comparison, the course of the mean monthly pressures for these cities over a number of years. From this comparison it clearly follows that



during the winter months, when the average pressure in Tomsk is considerably higher than in Moscow, the values of the critical frequencies in Tomsk are also considerably higher than in Moscow.

In summer-time, when the pressures at these points equalize, so do the critical frequencies.

This comparison quite convincingly shows that under identical conditions of illumination there is an equality of electron concentrations in the F_2-layer, and that with a relative increase in pressure and decrease in temperature, an increase in the electron concentration, analogous to the seasonal increase for a given point, is observed.

The data and considerations cited permit one to assert the existence of a continental effect in the geographic distribution of the electron concentration in the F_2-layer, the effect appearing in the enhancement of the seasonal effect in localities with a strongly pronounced continental climate. It is quite possible that the debatable conclusions on the presence of non-seasonal changes in the F_2-layer drawn by Berkner and Wells ([7];[8]) which were confirmed by Maeda and Tukada ([9]) and criticized by Kasantzev ([2]) and Likhachev ([5]), may be rejected on the basis of the data on the continental effect.

As a matter of fact, Berkner and Wells are to have drawn the conclusion regarding the existence of non-seasonal changes in the F_2-layer on the basis of a comparison of the course of the critical frequencies in Wateroo ($\varphi = 30°$ S) with the data for ionospheric stations of the northern hemisphere.

One may assume that the weakly defined seasonal dependence of the F_2-layer in Australia is due mainly to the weakly defined climatic difference between winter and summer.

The existence of the continental effect, which may be established on the basis of the observation data of ionospheric stations in the USSR, most favourably situated for disclosing this effect, confirms the statement of Martyn et al. ([4]) that there is a fundamental connexion between the seasonal effect in the F_2-layer and climatic conditions; and that the difference in the seasonal changes for various localities at the same latitude depends mainly upon the climatic conditions.

In conclusion we wish to express our deep gratitude to N. A. Korinevskaya and K. M. Kosikov for their help in obtaining the necessary data, and to D. N. Nasilov for discussing with us the meteorological aspects of the problem.

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CHEMISTRY

ON THE RÔLE OF DIFFUSION IN THE SOLID PHASE IN THE IONIC EXCHANGE BETWEEN THE PRECIPITATES OF SILVER HALIDES AND AQUEOUS SOLUTIONS

By A. POLESSITSKY and A. MURIN

(Communicated by V. G. Chlopin, Member of the Academy, 17.IV.1944)

The experiments of Kolthoff and O'Brien (1) and of A. Polessitsky (2) have established with the help of radioactive isotopes the fact of a rapid exchange of halogen ions between solutions of halides and all the mass of the precipitate of silver halide. A similar rapid exchange has been established by Langer (3) for silver ions. On the basis of the quantitative regularities of the exchange (influence of the surface of the precipitate, the rôle of the temperature), established by him; Langer has put forth the view that an essential rôle in the exchange process is played not by recrystallization, as has been assumed previously, but by the self-diffusion of the ions in the solid phase.

In this connexion it is of interest to compare the self-diffusion coefficients of silver ions in AgCl and AgBr that can be calculated from Langer's data for the exchange with the $AgNO_3$ solution on the assumption that all the effect observed is due to diffusion, with those coefficients which can be derived from direct measurements of the self-diffusion; and of the electrolytic conductivity due to it.

The self-diffusion coefficients of silver ions in AgCl and AgBr have been measured by Tubandt; Reinhold and Jost(4) with the help of isomorphic indicators at 238° C for AgCl and at 300° C for AgBr.

For AgCl $D^{Ag}_{238} = 1.8 \cdot 10^{-9}$ cm²/sec.; for AgBr as a mean for two indicators $D^{Ag}_{300} = 1 \cdot 10^{-8}$ cm²/sec.

In order to calculate the self-diffusion coefficients at 25° C measurements of the electrical conductivity can be used, since $\frac{D_{T_1}}{D_{T_2}} = \frac{\varkappa_{T_1}}{\varkappa_{T_2}} \frac{T_1}{T_2}$. The electrical conductivity of Ag^+ in AgCl at 238°C as a mean from the data of Lehfeldt (5), Tubandt and Lorenz (6) and Koch and Wagner (7) is $\varkappa_{238} = 5 \cdot 10^{-4}$. At 25° C, according to Lehfeldt, $\varkappa_{25} = 2 \cdot 10^{-7}$*, hence $D^{Ag\,(AgCl)}_{25} = 4 \cdot 10^{-13}$ cm²/sec.

The electrical conductivity of Ag^+ in AgBr at 300° C, according to the coinciding data of Lehfeldt, Koch and Wagner, and Tubandt and Lorenz, amounts to $\varkappa_{300} = 1 \cdot 10^{-2}$; at 25° C, according Lehfeldt's data, $\varkappa_{25} = 4 \cdot 10^{-8}$, hence $D^{Ag\,(AgBr)}_{25} = 2 \cdot 10^{-14}$ cm²/sec.

These magnitudes can be compared with those obtained from the data of Langer.

* This point lies on the gentle sloping «irreversible» part of the curve of electrical conductivity.

The degree of the exchange of silver ions between the solution and the precipitate reached during the time t is specified by the ratio

$$\alpha(t) = \frac{c(0) - c(t)}{c(0) - c(\infty)} \quad (1)$$

where $c(t)$ denotes the concentration of the radioactive Ag^+ ions in the solution (in the experiments of Langer the initial activity of the precipitate was equal to zero).

If the distribution of the concentration of radioactive silver in the solid phase is determined by self-diffusion, while the rapid surface exchange enables one to identify the relative concentration of radioactive ions of Ag^+ on the surface of the precipitate and in the solution, we have, as can easily be shown*

$$\alpha(t) = 1 - \frac{M_p + M_s}{M_p} \sum n_\lambda e^{-\lambda^2 Dt/R^2} \quad (t > 0) \quad (2)$$

where M_p and M_s are the mass of silver in the precipitate (p) and in the solution (s); D, the self-diffusion coefficient of the silver ions; R, the radius of the crystals of the precipitate (assumed to be spherical).

The characteristic numbers λ satisfy the equation

$$\operatorname{tg}\lambda = \frac{\lambda}{1 + \frac{1}{3}\frac{M_s}{M_p}\lambda^2} \quad (3)$$

while the coefficients n_λ can be calculated according to the formula

$$n_\lambda = 2\frac{\lambda\cos\lambda - \sin\lambda}{\frac{\sin 2\lambda}{2} - \frac{2\sin^2\lambda}{\lambda} + \lambda}\,\frac{\sin\lambda}{\lambda} \quad (4)$$

In order to estimate the self-diffusion coefficient of Ag^+ in silver chloride, we have used the results of those experiments of Langer ([3]) (with a fresh precipitate consisting of the smallest crystals) where $M_s/M_p = \frac{24.4}{19.8}$. In this case the equation (2) assumes the following form:

$$\alpha(t) = 1 - 0.49e^{-12.0Dt/R^2} - 0.18e^{-41.8Dt/R^2} \quad (2')$$

For $Dt/R^2 = 0.05$ we get $\alpha \simeq 0.71$. There follows from Langer's experiments that this degree of exchange is reached during the time $t \simeq 20$ minutes. Consequently, $D/R^2 = 4 \cdot 10^{-5}$ sec^{-1}.

Similar calculations, carried out for the case of the finest silver bromide precipitate ($M_s/M_p = 23.4/107.9$) have given for D/R^2 nearly the same value $4 \cdot 10^{-5}$ sec.$^{-1}$.

The value of the radius of the particles can be derived from Langer's data by means of the adsorption of the methylene blue. For both suspensions we are interested in, it amounts to 0.5 mg per m. equiv. of AgHal.

Putting for the methylene blue molecules $d^2 = 1 \cdot 10^{-14}$ cm, we get for the effective surface of 1 g precipitate (molecular weight of methylene blue = 380) $S_{\text{eff}}^{\text{AgCl}} = 5 \cdot 10^4$ cm^2 and $S_{\text{eff}}^{\text{AgBr}} = 4 \cdot 10^4$ cm^2, whence the effective radius of the particles (if the density of the salt is equal to 6) is found to be:

$$R_{\text{eff}}^{\text{AgCl}} = \frac{3}{6S} = 1 \cdot 10^{-5}\text{ cm};\quad R_{\text{eff}}^{\text{AgBr}} = 1.25 \cdot 10^{-5}\text{ cm}$$

These values are somewhat smaller than the geometrical radii, measured by Langer under the microscope, owing to the unevenness of the surface.

* The solution of the corresponding diffusion problem is not encountered in the literature.

The values D/R^2 and R^2 enable one to estimate D:

$$D_{25}^{Ag^+(AgCl)} \simeq 4 \cdot 10^{-15} \text{ cm}^2/\text{sec.}^{-1}; \quad D_{25}^{Ag^+(AgBr)} \simeq 6 \cdot 10^{-15} \text{ cm}^2/\text{sec}^{-1}$$

It should be noted that with the results of Langer's microscopic observations for the magnitude of the crystal radii of the AgCl precipitate ($R \simeq 0.5 \cdot 10^{-4}$ cm) we should get

$$D_{25}^{Ag^+(AgCl)} \simeq 10^{-13} \text{ cm}^2/\text{sec}^{-1}.$$

The preceding calculations have no other aim but to estimate the order of magnitude.

The exchange can thus be explained with values of the self-diffusion coefficients of the same order of magnitude at those derived from direct measurements of the mobility of silver ions in AgCl and AgBr (self-diffusion, electrical conductivity). It is clear that the self-diffusion in the solid phase can play an important rôle in the exchange of the silver ions.

On the other hand, the diffusion coefficients of the chloride and bromide ions at elevated temperatures are at least by a factor 1000 smaller than in the case of silver ions, and since the activation energy of the diffusion of halogen ions is higher than for silver ions, the difference will be still larger at low temperatures. No noticeable exchange of the halogen ions as a result of self-diffusion in the solid phase can therefore be expected; the rapid exchange established by Kolthoff and O'Brien, Polessitsky and Langer (according to Langer's data the rate of exchange for bromide ions being but 6 times smaller than for silver ions) is due to recrystallization which plays obviously an essential, although, apparently, not an exclusive rôle in the case of silver, too.

This conclusion is supported also by experiments with precipitates covered by a dye which, hindering the recrystallization, influences but slightly the exchange of silver ions and sharply decreases the exchange of bromide ions.

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PHYSICAL CHEMISTRY

ADSORPTION FROM SOLUTIONS AND THE MICROPOROSITY OF ACTIVATED CHARCOALS

By A. V. KISSELEV and K. D. SHCHERBAKOVA

(Communicated by M. M. Dubinin, Member of the Academy, 4.IV.1944)

No other adsorbent has been employed in adsorption studies so frequently as charcoal. And yet the information we have on the internal structure of charcoals is most meagre. The existing methods of determining the porosity of charcoals ([1],[2]) give only the total volume of the pores. Attempts to differentiate it with respect to pore-size were based on the application of conceptions of capillary condensation. However, the latter begins at relatively high vapour pressures, when the most active part of the volume of all the pores has already been filled up.

Non-activated sugar charcoals manifest a sharply expressed ultraporosity effect; and for them the heats of wetting in the series of fatty acids and alcohols ([3],[4]) and latter's adsorption from aqueous solutions ([5],[6]) increase in a reverse sequence to the «Traube series». As activation increases, this sequence changes; transforming into usual, «direct Traube series» ([7],[8]).

The concept of the «direct Traube series» in the sequence of magnitudes of the adsorption of surface-active substances from aqueous solutions was transferred from the interface solution—air to the interface solution—charcoal without sufficient criticism. This sequence is characteristic only for small concentrations. With an increase in the concentration of the organic substance in water; it is difficult to assume the formation of a monolayer on the charcoal. In the first place, in the adsorption potential of the charcoal with respect to the organic polar molecules the main rôle is played by the dispersion member ([9]) which has undergone extraordinary intensification in the fine pores and crevices ([10], [11]). Secondly; the interface film of organic molecules—aqueous solution possesses considerable free energy; and therefore with increasing concentration the organic substance in water will be easily «forced out» into the fine pores of the charcoal where the adsorption potential is especially high with respect to it. Increasing the polarity of the solution by introducing electrolytes leads to «salting out» ([12],[13]).

Monolayer adsorption from solutions of surface-active substances has been found so far only on the surfaces of liquids ([14], [15]) and on the surfaces of crystalline polar adsorbents ([16], [17]). In the case of finely porous silica gel there is a reversal of the «Traube series» in the region of maximum adsorption ([18]). One of the authors of this work has established that in the case of silica gel the maximum adsorbed volume is found to be independent of the length of the hydrocarbon radical of the molecules of the surface-active substance adsorbed; owing to their dense covering of the entire volume of the fine pores of this adsorbent ([20]).

These considerations compel us to study with special attention adsorption from solutions in the region of sufficiently high concentrations corresponding to saturation; *i. e.* maximum adsorption.

With a view to reaching a comparison of the maximum sorbed quantities of organic substances by the charcoal from aqueous solutions; we undertook an investigation of adsorption isotherms of the dissolved substances in as broad as possible a range of concentrations; striving to attain for diverse dissolved substances that region of concentrations in which adsorption already ceases to change; which enables us to avoid doubtful extrapolation.

It is absolutely clear that the distribution between the surface phase and the volume of the solution will in a marked degree depend upon the magnitude of the adsorption potential, and; hence; upon the magnitude of the hydrocarbon radical. Low-molecular fatty acids and alcohols which have a large generalized moment ([12]) at a given concentration will remain in the polar aqueous phase easier than high-molecular ones; which will be more intensively forced out upon the surface of the charcoal. This leads to the «direct Traube series», *i. e.* to an increase in adsorption with an increase in molecular weight. However; corresponding measurements were made in the region of quite small concentrations. Adsorption of low-molecular acids may likewise increase, only in this case a considerably greater increase in concentration is needed.

For the experiments samples of activated charcoal were employed from diverse specimens activated in the laboratory by water vapour up to a charring of 50 per cent. One of the specimens (No. 1) was treated with hydrochloric acid, extracted with alkali and washed with water, as a result of which its ash content fell to 0.06 per cent. Weighed samples of the dry charcoals in glass ampules were covered with the solutions and sealed off in air; since the adsorption of sufficiently high-molecular fatty acids does not change during evacuation ([19]). The ampules were shaken up until equilibrium was attained. The concentrations of the solutions before and after adsorption were found with the aid of an interferometer.

In the region of small concentrations sequence of the «direct Traube series» was found, as previously. However; in the region close to saturation of the charcoal we discovered that the adsorption of low-molecular acids not only rises to the magnitude of the adsorption of high-molecular ones, but exceeds the latter. Thus; there is obtained a converse picture to the adsorption from solution on liquid and non-porous surfaces; when the limiting maximum adsorption does not depend upon the length of the chain; and analogous to the case of adsorption on porous silica gel; when adsorption decreases with an increase in the radical. It is only natural; therefore; to seek an explanation of this fact in the influence of the dimensions of the pores. If we compute the maximum sorbing volume; *i. e.* if the maximum sorbing quantities are multiplied by the molecular volumes of the corresponding substances; we find the remarkable fact that whereas the maximum sorbing quantities of the molecules decrease with an increase in the hydrocarbon radical, the maximum sorbing volumes remain very nearly constant.

For the purpose of checking this fact; we strove to extend the number of substances employed. However, already octyl alcohol and caprilic acid are extremely slightly soluble in water. Therefore; we turned to salts of the higher fatty acids that dissolve better; namely; to sodium oleate and potassium erucate. A special investigation showed that fatty acids are selectively adsorbed by charcoal from such a solution; moreover; the adsorption reaches a maximum at small concentrations.

The results obtained for diverse specimens of activated charcoals gave the same picture—the maximum adsorbing volume, beginning with butyric acid, practically does not depend upon the length of the radical. Experiments with alcohols led to the same magnitude of the maximum adsorbing volume (see table).

By increasing the electric field of the solution by the addition of electrolytes it was found possible due to the surface salting-out effect to attain for low-molecular fatty acids also quite large magnitudes of adsorption at considerably smaller concentrations.

A study of the aromatic acids—benzoic and salicylic—led to an analogous picture.

We also investigated the adsorption of methylene blue and congo red from aqueous solutions. For them; however, maximum adsorbing volumes are less than for the fatty acids and alcohols, due to the fact that their particles may be very large.

The constancy of the maximum adsorbing volume for a homologous series of fatty acids and alcohols and the decrease in this magnitude for large particles of the dyes points to the influence of the fine structure of the pores. Possessing identical and quite small (some 20 Å²) cross-sections; the molecules of the homologous series of fatty acids and alcohols fill the volume of the pores during adsorption to a considerably greater extent than the large particles of the dyes.

Maximum Adsorbed Quantities of Fatty Acids and Alcohols from Aqueous Solutions by Activated Charcoal No. 1 (in mM/g and in cm³/g)

Acid	mM/g	cm³/g	Alcohol	mM/g	cm³/g
Acetic	(>3.24)	(>0.18)	Butyl	2.95	0.27
Propionic	(>3.17)	(>0.24)			
Butyric	3.20	0.29	Amyl	2.57	0.28
Valeric	2.59	0.28			
Capronic	2.24	0.28	Hexyl	2.23	0.28
Heptylic	2.02	0.29			
Oleic	0.83	0.25	Heptyl	1.92	0.27
Erucic	0.63	0.25			

Hence; we arrive at the possibility of estimating the volume in which adsorption of the dissolved substances takes place with respect to the quantities of the maximum adsorbing volumes of the latter. In the case of a homologous series of fatty acids and alcohols we obtain the largest volumes, corresponding to the densest covering of the adsorption field; this **constant maximum adsorbing volume** is determined by the structure of the adsorbent and represents the **volume of its micropores.**

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PHYSICAL CHEMISTRY

OXIDATION OF GASEOUS HYDROCARBONS

I. THE CATALYTIC ACTION OF WATER VAPOUR IN THE OXIDATION OF ETHANE

By N. CHIRKOV

(Communicated by N. N. Semenov, Member of the Academy, 29.III.1944)

In papers concerned with the oxidation of ethane there is one essential contradiction that attracted our attention.

Whereas in many of the kinetic curves given by Bone and Hill (1) the reaction rate maximum is pronouncedly shifted in the direction of small values of transformation; according to Steacie and Plawes' data (2) the reaction rate reaches a maximum when more than 50 per cent of the substance has reacted.

Highly interesting from the point of view of the theory of chain reactions are the comparatively rarely encountered kinetic curves in which the reaction rate maximum is pronouncedly shifted in the direction of per cent transformation greater than 50 per cent.

Experimental Procedure. The gaseous mixture $C_2H_6 + 3.5\ O_2$ studied was transferred with a measuring burette from a reservoir supply flask into a durobax glass reaction vessel (4.6 cm in diameter and 255 cm^3 in volume) placed in an electric oven. Connected with the reaction vessel was a highly sensitive membrane manometer with which the change in pressure in the course of reaction was registered (3).

To introduce into the reaction mixture water vapour up to a pressure higher than the vapour pressure of water at room temperature, a glass tube of very small volume with a previously calculated quantity of water was sealed to the reaction vessel; while evacuating the air from the reaction vessel; the water in the glass tube was frozen by immersing the latter into a Dewar flask containing liquid air. When it was necessary to evaporate the water into the reaction space from the glass tube the latter was heated with a burner or an electric oven. To keep the water vapour introduced in this manner from condensing on the cold parts of the connecting tubing, a small amount of oxygen was introduced into the reaction vessel beforehand; the small diameter of the connecting tubing (1.2 mm) prevented diffusion of the water vapour and its condensation on the cold parts.

Experimental Results. In Fig. 1 is given a graph of the increase in pressure with time for three experiments at $T = 486°$ C and pressures of: *I* — 322 mm; *II* — 196 mm; *III* — 137 mm. The time is expressed in minutes and the pressure in millimeters.

The given curves differ from the symmetrical S-shaped curves, most frequently of all encountered in kinetics; in that they are asymmetrical with respect to the time of 50 per cent transformation; namely: according to our curves the first 50 per cent of the substance reacts in an incomparably greater interval of time than the second half of the substance. That is why our curves are more like those of Steacie and Plawes' than Bone and Hill's.

The asymmetry stands out still more strikingly if the kinetic curves are plotted in the coordinates «reaction rate—quantity of substance that has reacted».

Since we had a very sensitive membrane manometer, the rate (dp/dt) could be computed with a high degree of accuracy.

In Fig. 2 the dependence of the reaction rate upon Δp, which is equivalent to the dependence upon the quantity of substance that has reacted for the curves of Fig. 1, is represented by dots.

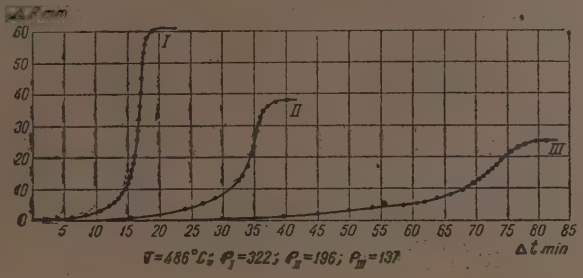

Fig. 1

As we see, the reaction rate, regardless of the pressure; reaches a maximum when 70 per cent has reacted and not 50 per cent as in the case of symmetrical S-shaped curves.

The dependence of the reaction rate upon the quantity of the substance that has reacted is well described by the empirical formula:

$$\frac{d\eta}{dt} = k\,(e^{B\eta} - 1)\,(1 - \eta)\,\eta \qquad (1)$$

or; in the first approximation;

$$\frac{d\eta}{dt} = k_1\eta^2\,(1 - \eta) \qquad (1')$$

where $\eta = \Delta p / \Delta p_0$ is the quantity of substance that has reacted referred to complete transformation, and k and B are reaction constants.

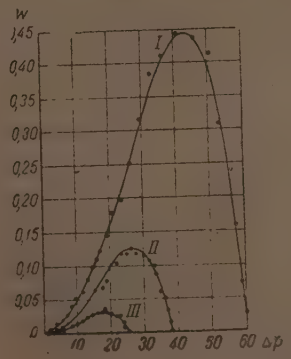

Fig. 2

In Fig. 2 the curves represented by straight lines correspond to formula (1) for $B = 1.5$ and $k = 1.15$; 0.26; 0.078; for the three pressures studied respectively, if dp/dt is expressed in mm/sec.

The fact that the experimental points coincide with the calculated curves confirms the soundness of equation (1).

The maximum rate is proportional; in the first approximation; to the cube of the initial pressure of the reacting gases.

Catalytic Action of Water Vapour. Equation (1), formally speaking, is autocatalytic; *i. e.* the reaction rate increases with an increase in η; the magnitude of which varies directly as the quantity of the end products. However, cases are very frequent when this evidence is purely formal; for accumulation of the end products does not accelerate the reaction. With view to elucidate the influence of the end products upon the reaction; we added CO_2 and H_2O to the initial mixture. It was found that CO_2; at least in small amounts; has no effect at all upon the reaction rate; water vapour, on the other hand; greatly accelerates it. This

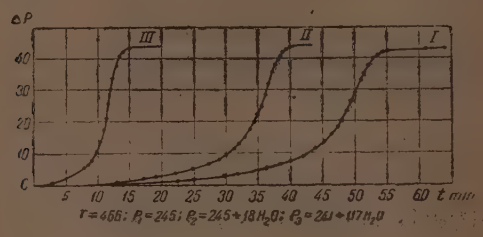

Fig. 3

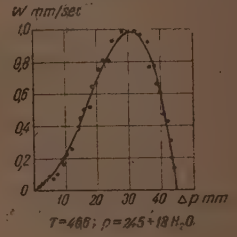

Fig. 4

accelerating action of water is shown in Fig. 3: curve *I* is a pure mixture of $C_2H_6 + 3.5\ O_2$ at $p = 242$ mm and $T = 466°$ C. Curve *II* represents the addition of 18 mm of H_2O to the pressure of the stoicheiometric mixture. Curve *III*; the addition of 117 mm of H_2O. In spite of such a strong catalytic action of water; it is impossible to explain the acceleration of the reaction only as due to catalysis by water. Were it so, indeed; then with such large additions of water as in experiment *III* (Fig. 3) the reaction should have begun with an extremely high initial rate; close to the maximum, whereas in reality the initial rate is close to zero.

Hence the acceleration of the reaction is evoked not only by the water that forms, but also by some other substances which are intermediate products. The right part of equation (1) consists of the product of three terms; moreover; with an increase in η two of the terms increase, producing a positive acceleration. We will assume that the accelerating action of water is mathematically expressed only through one of the terms, namely, η. When water is added to the reaction mixture beforehand, its amount x, expressed in relative units, must be added to the term η in equation (1) which then becomes:

$$\frac{d\eta}{dt} = k\,(e^{B\eta} - 1)\,(1 - \eta)\,(\eta + x) \qquad (2)$$

x is the ratio of the water added to the reaction mixture to the maximum possible quantity of water that forms in the experiment; in determining x we assumed that during reaction all the hydrogen is oxidized to water. For experiment *II* (Fig. 3) equation (2) is rewritten in the form

$$\frac{d\eta}{dt} = 2.2\,(e^{1.5\eta} - 1)\,(1 - \eta)\,(\eta + 0.11) \qquad (3)$$

where $k = 2.2$ was found from the magnitude of the maximum rate. This equation which is graphically represented in Fig. 4, coincides completely with the experimental data.

Conclusions. It has been shown that in the oxidation of ethane in stoicheiometric proportions with oxygen:

1. The reaction rate at a temperature of 466 and 486° C depends upon the quantity of the substance that has reacted and upon the quantity of water vapour added according to the empirical equation (3).

2. From the equation found it follows that:

a) it is impossible to explain the acceleration of the reaction by the catalytic action of water alone, some kind of intermediate products exist that cause the reaction to pick up speed (since the end products, except for H_2O, do not accelerate it);

b) in accordance with experiment the reaction rate reaches a maximum when 70 per cent of the substance has reacted.

3. The discrepancy between our kinetic curves and those of Bone and Hill is perhaps due to the different temperatures at which the experiments were carried out. Only additional experiments can settle this question.

The question of the theoretical interpretation of the catalyzing action of water, just as in our experiments on studying the reaction $H_2 + O_2$[3]; has not been cleared up yet.

However, in solving the basic question as to where the catalyzing action of water manifests itself; on the surface or in the volume, attention should be paid to the proportionality between the reaction rate and the quantity of water (introduced and formed) up to quite large values of the latter.

It is impossible to explain this fact by the catalytic action of water adsorbed on the surface.

It is more probable that catalysis by water takes place in a homogeneous manner.

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GEOCHEMISTRY

ON THE ORIGIN OF THE PRINCIPAL TYPES OF MINERALIZED WATERS IN SEDIMENTARY ROCKS

By A. N. BUNEEV

(Communicated by V. G. Chlopin, Member of the Academy, 31.III.1944)

The problem of the origin of mineralized natural waters is intimately related to the history of sea water and its salts in the zone of sedimentation and in the stratisphere since the moment of its capture by sedimentary deposits. These first buried waters of sedimentary formations may occur as mobile waters filling water-permeable rocks, and as immobile capillary waters of fine-grained and clayey rocks.

Buried waters of sedimentation have existed during an indefinitely long time, and their decomposition does not take place unless, as a result of geotectonic processes a possibility arises of their replacement by waters of atmospheric origin. Slightly mobile capillary waters have existed for a still longer time; and their composition at the contact with the horizons of infiltration of atmospheric waters changes but very slowly under the effect of the thermal movement of ions (diffusion) (1).

We are facing a geochemical problem of finding the main trends of the metamorphization of the ionic composition: 1) of the waters of epicontinental seas, 2) of those in marine sediments; 3) of the waters contained in rocks at later stages of their existence; 4) of the waters originating in the process of leaching-out of sedimentary rocks of marine origin. The analysis of the problem brings us to the following conclusions:

1. The process of terrigenous accumulation of sediments is always accompanied by a change in the sea waters; becoming higher in $Ca^{\cdot\cdot}$ ions and lower in $Na^{\cdot}$ and SO_4'' ions. At the basis of metamorphization lies a colloidal-chemical process of exchange adsorption of cations, taking place as a result of a shifting of the clayey material from the dry land where it was in equilibrium with the waters of the dry land ($Ca^{\cdot\cdot}$ predominating) to the sea where it attains equilibrium with sea water (in which $Na^{\cdot}$ is valent):

$$2NaCl + Ca\,(adsorb.) \rightleftarrows CaCl_2 + Na_2\,(adsorb.)$$

In this process all the cationic ratios (in per cent equivalent to their sum) of sea water ($Na^{\cdot} + K^{\cdot}$; 78.6 per cent; $Mg^{\cdot\cdot}$, —17.8; $Ca^{\cdot\cdot}$, 3.5) undergo a change; approaching the cationic ratios characteristic of the waters of the dry land ($Na^{\cdot} + K^{\cdot}$, 18.0 per cent; $Mg^{\cdot\cdot}$, 17.5; $Ca^{\cdot\cdot}$, 64.0).

Under the present conditions this process is observed in near-sea lakes (2); on a small scale; it is true; but from the standpoint of its chemistry qualitatively corresponding to the one described. In the geological past; it must have been manifested on a large scale in shallow-water seas of the epochs of extensive transgressions; accompanying the accumulation of terrigenous deposits of great thickness in geosynclines.

The metamorphization of water in these areas told upon the whole of the basin; bringing about the formation of «chlorine-calcium» seas with a low $Na^{\cdot}/Cl'$ ratio (< 0.85), a low sulphate content (precipitation of gypsum) and a varying degree of mineralization (surface concentrating). The probability of the formation of this type of seas is in agreement with the run of the curve of epeirogenetic oscillations of the Earth's surface; corresponding to the areas of its negative movements; since the end of the Palaeogene (a rise of the curve) no conditions have existed for an extensive development of calcium seas.

At the epochs of regressions the metamorphization of the waters assumes a different; reverse course. In the residual basins of the sea; becoming gradually reduced in size; there accumulate salts washed away by the atmospheric waters from the surface of the areas of exposed marine sediments. In these basins are collected also $Na^{\cdot}$ ions; and partly $Mg^{\cdot\cdot}$ ions adsorbed in sediments; now they pass again to a state of equilibrium, in accordance with the dry land conditions:

$$CaSO_4 + Na_2\,(adsorb.) \rightleftarrows Na_2SO_4 + Ca\,(adsorb.)$$

$$Ca(HCO_3)_2 + Na_2\,(adsorb.) \rightleftarrows 2NaHCO_3 + Ca\,(adsorb.)$$

The waters of the residual sea basins pass to the type of the chloride-sulphate- or chloride-hydrocarbonate-sodium waters with a $Na^{\cdot}/Cl' > 1$ ratio. The probability of the formation of basins of this type corresponds to the areas of the rise of the curve of epeirogenetic movements; under the present conditions this process is observed in continental lakes and «seas» (the Caspian) formed in the belt of dry climate as a result of leaching-out of sediments of the regressing seas of the Tertiary and Quaternary ([2]). As an intermediate type basins may originate with a $Na^{\cdot}/Cl'$ ratio $= 1$; poor in $Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ (precipitation of carbonates and sulphates). For all the three types the Br'/Cl' ratio is near the normal oceanic ratio (~ 0.0015)*.

All the three types of water in a buried form pass to the stratisphere, being retained in the sediments.

2. In coarse grained sediments, containing neither a colloidal complex nor organic substances; the buried solutions can change but very slightly. In the presence of organic matter the biochemical processes of sulphate-reduction lead to an accumulation of H_2S; a replacement of the SO_4'' ions by HCO'_3 and CO''_3 ions and to a shifting of the pH towards the alkaline side. The HCO'_3/Cl' ratio approaches the SO''_4/Cl' ratio (equiv.) in the original water of the basin: in the normal sea waters it is ~ 0.1; in chloride-sodium-calcium, < 0.1; and in chloride-sulphate waters of regressing basins; > 0.1. The accumulation of CO_3'' ions brings about a removal from the solution and the colloidal complex of $Ca^{\cdot\cdot}$ ions; precipitated as $CaCO_3$; a part of the $Na^{\cdot}$ and $Mg^{\cdot\cdot}$ ions is adsorbed in place of Ca; in addition; magnesium falls out also as a carbonate.

3. The degree of the transformation of the buried solutions within the subsequent time of the existence of the rock (above the zone of metamorphism); which is enormous as compared to the silt-stage; must; however; be insignificant because of the dying-out and inhibition of the bioprocesses that take place even in the deeper layers of the silts.

4. The process of leaching-out of sedimentary marine rocks; taking place since the moment of replacement of the mobile buried waters by atmospheric waters, brings about a diffusive equalization of their ionic concentrations with the immobile capillary waters. The total mineralization of the leaching waters formed decreases as the process advances; and the predominant part in the solution is played by the ions of slightly soluble salts (gypsum; carbonates): $Ca^{\cdot\cdot}$; SO''_4; HCO'_3. In the clayey rocks; into solution simultaneously pass adsorbed ions of $Na^{\cdot}$; $Mg^{\cdot\cdot}$; and the water is metamorphized into a low-mineralized chloride-sulphate or chloride-hydrocarbonate-sodium type of waters.

Still later sulphate- or hydrocarbonate-calcium-sodium waters; and; finally; fresh waters are formed.

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* When rock salt is leached out, waters with a very low Br'/Cl' ratio are formed.

5. The mineralized chloride-sodium-calcium; or chloride-hydrocarbonate-sodium waters; widely distributed in the stratisphere and particularly interesting owing to their frequent association with petroleums; correspond to the buried waters of the two above-mentioned types (the «chlorine-calcium» waters of a regional distribution from the genetic standpoint can be nothing else than remains of waters of the corresponding epicontinental seas; the hydrocarbonate-sodium waters can also originate at definite stages of leaching of marine sediments).

The two types of waters refer to the «petroleum waters»; since both the conditions of their formation and those of their preservation (as buried waters) are similar to the conditions of formation and preservation of petroleums. The probability of their association with petroleums sharply increases when ions and molecules of biogenic origin are present: H_2S; $NH_4^{\cdot}$; I', hydrocarbons; *etc.*

6. Particular importance in the study of the ionic-salt complex of sedimentary rocks, with a view of retracing the physical-geographical conditions of their formation; should be attached to the study of the composition of capillary waters (1) and of the Br'/Cl' ratio in the sea water; until the beginning of the NaCl crystallization remains steady and near the oceanic one—0.0045 (equiv.) (3). A study of the concentration of Cl' and of the Br'/Cl' ratio in immobile (capillary) waters of the sediments in basins which become shallower and whose area decreases; may facilitate the retracing of the process of alteration of the shore-line; and reveal the probable areas of halogenesis. Finally; the material necessary to form an idea as to the composition of the waters of seas and oceans at the past geological epochs cannot be collected unless a thoroughgoing study is made of the ionic-salt complex of sedimentary rocks against the background of their geological history. The organization of systematic work along this line is of great interest both from the scientific and the practical standpoint.

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GEOLOGY

A CONTRIBUTION TO THE CHARACTERISTIC OF THE HYDROCHEMICAL FACIES OF THE EDGE WATERS OF THE STRATISPHERE

By G. A. MAXIMOVICH

(Communicated by F. P. Savarensky, Member of the Academy, 1.IV.1944)

The waters of the stratisphere are represented by three main types of edge waters: surface waters, artesian epigenetic, and artesian syngenetic waters.

The surface edge waters occur above the surface of erosion. They are common, *e. g.*; in the Mesozoic cover of the Russian platform. Unfortunately; hydrochemical data concerning these waters are very scanty.

Somewhat better studied are the artesian waters of the stratisphere. The investigations carried out during this century have shown that the concentration and chemical composition of waters from the same bed change with depth from its exposures ([9], [12], [30], [37], [40], [42]). It is therefore possible to speak of hydrochemical facies in connexion with the edge waters of the stratisphere, not only those in the pore spaces; but also such as are confined to a system of communicating fractures, as well as for river waters ([28]).

A hydrochemical facies of edge waters is an area of the water-bearing bed (or a series of beds) distinguished throughout by identical hydrochemical conditions, which may be determined according to the predominance of definite dissolved components (ions; colloids). The concentration and mineral composition of the water of each of these areas varies within a certain range; but the predominance of the same substances persists. Just as in the case of river waters, the hydrochemical facies is determined according to the three components prevailing by weight, and the name given to it is composed of the names of these components in the decreasing order of their value. The change in the chemical composition of river waters as dependent on their concentration has been discussed in a previous note by the same author ([29]).

For the waters of the stratisphere the same regularity holds in its main features ([42], [9], [12]). To each concentration of edge waters in most cases corresponds a definite composition; a definite facies.

The stratisphere is characterized not only by the same hydrochemical facies as the river, lacustrine and ground waters; but also by some new ones. The occurrence of waters in the pore spaces of the beds, without any communication with the atmosphere above the Earth; in the Earth's crust characterized by peculiar thermodynamic conditions, produces new manifestations of the system: rock ⟷ water ⟷ gas ⟷ living matter, or of the hydrochemical facies.

The hydrochemical facies of edge waters of the stratisphere belong to four formations (groups): the hydrocarbonate, the sulphate; the sodium and the chloride one, determined after the first component prevailing by weight. They are listed in the table.

Main Hydrochemical Facies of the Edge Waters of the Stratisphere

Groups of facies (formations)	Facies
Hydrocarbonate	HCO_3—Ca—Na, HCO_3—Ca—SO_4, HCO_3—Ca—Cl, HCO_3—Ca—Mg, HCO_3—SO_4—Ca, HCO_3—SO_4—Cl, HCO_3—SO_4—Na, HCO_3—SO_4—Mg, HCO_3—Na—Ca, HCO_3—Na—SO_4, HCO_3—Na—Cl(+SO_4) sulphate, HCO_3—Na—Cl(—SO_4) not-sulphate, HCO_3—Cl—Ca
Sulphate	SO_4—HCO_3—Na, SO_4—HCO_3—Ca, SO_4—Ca—HCO_3, SO_4—Ca—Na, SO_4—Ca—Cl, SO_4—Cl—Na, SO_4—Na—HCO_3, SO_4—Na—Ca, SO_4—Na—Cl
Sodium	Na—HCO_3—SO_4, Na—HCO_3—Cl(+SO_4), Na—HCO_3—Cl(—SO_4), Na—SO_4—HCO_3, Na—SO_4—Cl, Na—Cl—HCO_3(+SO_4), Na—Cl—HCO_3(—SO_4), Na—Cl—SO_4
Chloride	Cl—HCO_3—SO_4, Cl—HCO_3—Na, Cl—SO_4—Na, Cl—Na—HCO_3(+SO_4), Cl—Na—HCO_3(—SO_4), Cl—Na—SO_4, Cl—Na—Ca(+SO_4), Cl—Na—Ca(—SO_4), Cl—Na—Mg

The hydrocarbonate facies are characteristic of the slightly concentrated epigenetic waters and are commonly used for water supply purposes. These may be both surface and artesian edge waters.

The hydrocarbonate-calcium facies are quite common among the Jurassic and Cenomanian water-bearing horizons of the North-Ukrainian trough ([30]), in the Upper Carboniferous deposits of the Moscow Palaeozoic depression ([9]), in the Paris; Dakota; Wisconsin basins; and in a number of other places.

The hydrocarbonate facies, with increasing distance from the exposure of the bed at the surface or in less permeable; *i. e.* less mobile areas; with an increase of mineralization are replaced by sulphate facies. This phenomenon has been observed both in the Moscow and in the North-Ukrainian basins.

The presence of unleached sulphates and chlorides within the stratisphere causes the appearance among slightly mobile edge and fissure waters of the sulphate and chloride facies. Thus; the slightly concentrated epigenetic atmogenous waters of the stratisphere change; according to the same general laws as the surface waters.

With growing depth from the exposure of the bed at the surface; a gradual change of facies is observed: $HCO_3 \rightarrow Ca—SO_4 \rightarrow HCO_3 \rightarrow SO_4—Ca \rightarrow SO_4—HCO_3—Ca \rightarrow \rightarrow SO_4—Ca—HCO_3 \rightarrow SO_4—Ca—Na \rightarrow SO_4—Cl—Na \rightarrow Cl—SO_4—Na \rightarrow Cl—Na—Ca (+SO_4) \rightarrow Cl—Na—Ca(—SO_4)$.

This change of hydrochemical facies is traceable in the Moscow basin ([9]) and at Levshino ([12]). The local phenomena; as for example; the development of enriched magnesium ores; may sometimes cause the appearance of a specific hydrocarbonate-calcium-magnesium facies. Such are *e. g.* the waters of the Middle Carboniferous of the Moscow depression ([9]).

The edge waters of the stratisphere are characterized also by new facies which were absent in surface and ground waters. The principal distinction of the waters of the stratisphere is their gas composition ([2]). The underground atmosphere of edge waters is different in composition from the gases of the river; lacustrine and ground waters; a considerable part of which occur above the level of the oxygen surface. In the composition of the underground atmosphere of the edge waters of the stratisphere a predominant part is played by nitrogen; carbon dioxide; hydrocarbons and hydrogen sulphide, in a different facial environment; at different stages of metamorphization of the epigenetic and syngenetic waters and their mixtures: An enrichment in helium permits to determine the age of the waters from the helium to argon ratio ([32]).

The waters of the pore beds of the stratisphere; changing their place very slowly, are of a higher concentration. A saturation with the most sparingly soluble compounds causes a precipitation in the form of cement of silica; calcium carbonate and

calcium sulphate. This is a feature common both to the waters of the stratisphere and to those of lakes.

The anaerobic conditions are the cause of the existence of a peculiar underground biosphere (of the geosphere, and not of the shell ([6–9, 34, 35])). In the waters of the stratisphere, under suitable conditions, the processes of desulphation and denitrification are rather extensively developed ([1, 10, 11, 13, 31, 34–39]). Under the influence of bacterial processes the syngenetic and epigenetic waters of the stratisphere are transformed.

The edge waters of the stratisphere are formed at the expense of two main sources—of syngenetic pelogenic waters ([2–4]) and epigenetic atmogenous waters, as well as potamogenic, thalassogenic and limnogenic ones. According to the geological history of a given area of the Earth's crust; in the bed the syngenetic pelogenic waters are either preserved or gradually replaced by epigenetic waters of a different origin. In different stages of the development of the structure of the Earth's crust different stages of replacement of syngenetic waters by epigenetic ones are observed. These stages of replacement are reflected in a different concentration of the edge waters; in the diversity of the hydrochemical facies.

The edge waters may be monofacial. Such are the syngenetic waters of the Berea sandstone in the Appalachians; represented by the chloride-sodium-calcium facies with no sulphate ([42]). Likewise monofacial are not infrequently the surface waters of the stratisphere; belonging to the hydrocarbonate-calcium facies.

In most cases the edge waters of the stratisphere are polyfacial. Both the epigenetic waters infiltrating to the bed; and the mixture of the epigenetic and syngenetic waters give a comparatively great variety of hydrochemical facies; changing in a regular way with the advance from the exposures of the bed deeper into the Earth's crust ([9, 12]).

In addition to a change in the hydrochemical facies in the horizontal direction; they also change along the vertical. The nature of this change depends on the geotectonical setting, geomorphological conditions, development of denudation processes and disjunctive dislocations; and the permeability of the beds.

Under platform conditions the intensity of the movement of the waters diminishes with depth; and along the vertical an increase of the concentration of the solutions is noted; with a corresponding regular change in the hydrochemical facies. This is true of the Palaeozoic waters of the near-Ural; Volga and Emba regions ([24, 26, 27, 33]).

In geoanticline areas; under conditions of a dissected relief, the permeability determines the different relations between the hydrochemical facies. Such is the case both in the Grozny region, and in the Daghestan region, in the Apsheron peninsula; in California, in the Rocky Mountains ([5, 14–25, 33, 38, 40–41]).

In the Grozny region a decrease is observed in the concentration of the waters from the Sarmatian deposits towards the Karagan and Chokrak deposits; and an increase is noted again in the Maikop deposits. This reflects the preservation of syngenetic waters ($Cl—Na—Ca(—SO_4)$) in the Sarmatian and Maikop and the existence of epigenetic waters and of mixed ones between these two. In the Apsheron peninsula the mineralization diminishes from the Apsheronian and Akchagylian and the upper portion of the productive series towards the lower part of the latter. This corresponds to the replacement of the syngenetic waters by epigenetic and mixed ones. In Daghestan an inverse relation as compared to the Apsheron peninsula is observed in Kai-Kent and Berekey.

The activity of man who exposes the stratisphere by mines and holes results in the appearance of new types of underground waters; and alters the rate of the movement of the edge waters.

By means of wells man unites beds with different hydrochemical facies and makes appear in the field of development of one facies oases centres, spots of another one. Such phenomena are of frequent occurrence in oil fields. As a result of oil mining in the Grozny region the abundant hot springs of Goryachevodsk have ceased to exist. The upper horizons of the Grozny region, like those in a number of other oil provinces; that have been made to com-

municate through a large number of wells; present a mixture of different waters of different hydrochemical facies.

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MINERALOGY.

COLOURED HALOES AROUND MONAZITE INCLUSIONS IN QUARTZ

By G. G. LAEMMLEIN

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The haloes described have been discovered in some crystals of zonally coloured smoky quartz from the veins of the Antonova Gora mine (Transbaikal)*. The haloes are spherical continuous smoky spots of different size (0.5—6 mm in diameter), visible to the unaided eye. Each halo has in its centre one crystal, less frequently a group of crystals (0.1—1 mm in diameter), these are evidently the source of the radiation responsible for the coloration of the halo. One is at once struck by the fact that the size of the haloes is proportional to that of the inclusions. The colour of the halo, which is the deepest near the centre, is gradually fading towards the periphery. The boundary of the halo is not a sharp one, but is distinct enough to make it possible to evaluate the dimensions of the haloes. The variations in the size and the diffuseness of the boundaries, as well as the absolute dimensions of the spherical haloes sharply distinguish them from the well-known concentric haloes due to the path of α-particles in fluorite, biotite and other minerals.

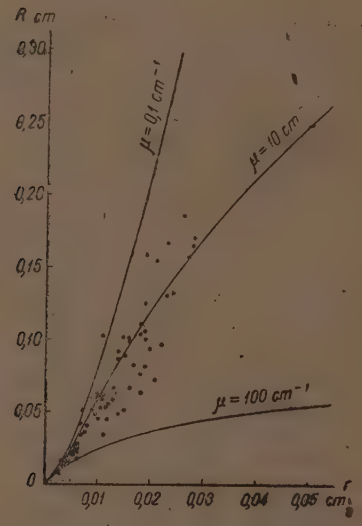
The mineral producing haloes was deposited on the quartz crystals growing from the walls of the vein fissures in the form of already existing small crystals. They were settling only on crystal faces turned upwards. Because of the zonal coloration of quartz with haloes; the mode of its growth can well be determined at the moments of deposition of the included crystals according to these zones. The crystals are enclosed in layers which have been deposited after the stop in the growth or even temporary dissolution of the quartz; apparently as a result of microtectonic causes. The quartz layer itself is coloured throughout, although much less intensely than the haloes. It is essential to note that the corresponding layers which have grown over the faces turned downward, are also coloured. This should be taken to mean that the potential coloration of the quartz layers has been made visible by a radiation of an active impurity absorbed directly by the quartz lattice. The action of X-rays may stimulate the coloration in a number of zones of crystals which remained colourless heretofore, containing no active impurity.

The included mineral yields a reaction for phosphorus and; according to the spectrum of absorption; contains elements of rare earths of the cerium group (1). It is honey-yellow in colour. The small crystals are well developed; nearly isometrical. A crystal opened by grounding gave during 30 days of exposure through a cellophane coating a distinct uniform radiograph on a negative photofilm. The mineral can be determined as monazite which is known to carry up to 15—20 per cent of Th.

From the spherical shape of the haloes it may be seen that the properties of the field of radiation produced around the monazite approach those of the central

* The specimens have been obtained from L. E. Kule.

field. Therefore it may be assumed in first approximation that the intensity of radiation around the source of β- or γ-rays decreases with the distance from the centre of the inclusion; in accordance to the law of inverse squares and to the simple exponential law of absorption, and the intensity of the coloration produced is directly proportional to the intensity and time of radiation. A calculation shows that the sharpness of the outlines of a wide halo increases along with the exponential coefficient.



On the other hand; an increase in absorption obviously reduces the limiting dimensions of the halo. As the boundaries of the haloes in quartz are sufficiently distinct; and assuming that γ-rays would give diffuse haloes; I believe that the haloes here described are due to hard β-rays. In the subsequent calculations the approximate value of the absorption coefficient of hard β-rays in quartz is put at $\mu = 10\ cm^{-1}$ (for comparison sake for medium β-rays μ is put at 100 cm^{-1}; and for γ-rays at 0.1 cm^{-1}). Within a certain distance from the centre of the halo its optical density remains practically unchanged. This distance may be considered as the radius of the halo.

The apparent value of the radius of the β-halo depends on the quantity of the radiating substance; time of action; absorption coefficient μ, and the sensibilization coefficient specific for the given specimen; characterizing its ability of being coloured; as well as on the contrasts of eye sensitivity. The radii of the haloes produced simultaneously around sources of different intensity depend on the size of the source. In a more sensitive medium the same source will; however; produce a halo with a larger diameter than in a less strongly sensibilized medium. Thus; it is sometimes observed that monazite inclusions lying at the boundary of layers assuming a smoky or a yellow coloration; give to the smoky layer a zone of coloration nearly by one third wider than in an adjacent layer; taking a yellowish colour.

Or else the coloration appears in some particularly sensibilized layers of the crystal far beyond the boundaries of the halo itself.

If we are to assume that the optical density, D, of the halo within a distance x from the source of radiation Q_0 will be $D_x \sim \frac{Q_0}{R^2} e^{-\mu x}$, then taking a certain threshold value of the density at the boundary of the halo; D_R; it is possible (for haloes of the same age) to determine the radii R of the haloes formed around inclusions with radii r (*i. e.* sources of different intensity), using a graph constructed according to the following formula:

$$r \simeq \sqrt[3]{kR^2 e^{\mu R}}$$

The coefficient k contains the following constants; partly specific for every specimen: 1) the relative content of active matter in the inclusions; 2) the exponential coefficient, similar for all the inclusions of the same age, showing the amount of the disintegrated matter; 3) the coefficient characterizing the sensitivity of the lattice to the radiation; 4) here enter also the constant value $\left(\frac{4}{3}\pi\right)$ and the reverse value of the threshold (marginal) optical density of the halo.

The figure shows three curves of the dependence of R on r; calculated with the aid of arbitrarily chosen coefficient for γ-rays, for hard and medium β-rays. In the same diagram are plotted points corresponding to 70 measurements of R and

r of the haloes which fit best into the shape of the curve for hard β-rays; reflecting the dependence of the β-halo both on the size of the inclusion and on the exponential coefficient of absorption. The scattering of the points observed about the theoretical curve calculated for hard β-rays may be explained by: 1) errors in the visual determination of the haloes' boundaries; 2) errors in the determination of the average size of the inclusion; 3) a possible dissimilarity of Th per cent content in different monazite crystals; 4) a different degree of sensibilization of the quartz crystal lattice around different inclusions. The systematic deflections from the curve may be due to: 1) the fact that the inclusions are not a point-shaped source of radiation; 2) the unhomogeneity of the β-radiation; 3) to the fact that the absorption of β-rays is actually not determined by a simple exponential law; *etc.*

It would be tempting to use the β-haloes in quartz for determining geological age; as it is done with α-haloes; though; like all the secondary radioactivity methods of determination of geological age; the method of β-haloes must have all the drawbacks known to be inherent in the method of α-haloes [2], not to speak of the fact that the value of the radius of the β-halo itself defies accurate measurement.

If the amount of active matter present in the inclusion Q_t is determined, the optical density $D_{R,t}$ at a distance R will within a time t be

$$D_{R,t} \sim \frac{Q_t}{R^3}(e^{\lambda t} - 1)\, e^{-\mu R}$$

Hence, from the value of the radius of the halo by the time t we shall find that the time t is equal to

$$t \simeq \tau \ln [(k' Q_t^{-1} R^3 e^{\mu R}) + 1]$$

Consequently; knowing the constant $\tau = 1/\lambda$ (λ is the constant of decay), we shall determine Q_t having measured the R haloes; and having found experimentally; with a suitable standard preparation the coefficient k' for a given specimen; it will be possible to attempt an approximate calculation of the lower limit of the time t necessary for the formation of the halo measured.

The coloured haloes around monazite inclusions in quartz here described are the first example known of natural colouring of quartz under the effect of β-rays. Similar haloes were also observed around orthite inclusions in certain high quartzes from Volyn pegmatites. Aside from age determination; a more detailed study of the structure of β-haloes may shed light upon some other obscure points in quartz coloration.

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PLANT PHYSIOLOGY

PHOTOSYNTHESIS AND GROWTH-PROCESSES IN BEET (*BETA VULGARIS* L.)

By A. A. RICHTER, Member of the Academy, K. T. SUKHORUKOV and L. A. OSTAPENKO

The conversion of CO_2 and of water into organic substances has of late been the subject of numerous investigations. Within recently many a students have taken interest in photosynthesis under its photochemical aspect which is far from having received a thoroughgoing interpretation as yet (1,2). Comparatively few have been engaged; however; in the study of the photosynthesis physiology proper in connexion with the physiological activity of the plant itself.

Among the problems of the physiology of photosynthesis that claim to an immediate solution should be classed the one of the relation between the processes taking place in a green plastid and those going on in the surrounding plasm; in other words; the relation between the synthesis in the strict sense of the word and the other vital processes taking place in the cell and in the plant as a whole.

It is interesting to mention that the process of synthesis of organic matter in a green plant did not seem fully clear to K. A. Timiriazev (3) who referred this problem to the future of plant physiology.

What is obscure in the question we have set before ourselves are the respective rôles played by the plastids and by the plasm in the synthesis of organic matter. It is necessary to find out the point where ceases the work of the plastids and where the reactions in the cytoplasm set in; or else we are brought to conclude that all the reactions of photosynthesis; both in the plastids and in the plasm; are mutually related; leading ultimately to a functional entity; or to the «polyplasm»; in the sense given to this term by Pantanelli (4).

Two tendencies may be distinguished in the physiological literature. One of them may well be expressed in the following words belonging to Lubimenko (5): «the photosynthesis as a physiological function of plant's nutrition is in the first line controlled; irrespective of any possible combination of accessory external and internal agents; by the requirements of the organism as a whole». A different opinion has been expressed by Kostychev (6) who studied photosynthesis in leaves of various plants; traumatized by pricking; the photosynthesis was found to be but slightly affected in them; which; according to the author; testified to the process of photosynthesis being independent of the plasm. Kostychev's view may be found in any cumulative textbook (7).

We believe the existence of these two conflicting opinions to be due to a different approach to photosynthesis; interpreted in its strict or wide sense.

One may agree with Lubimenko (5) that two phases are to be distinguished in the process of photosynthesis; as understood in its wide sense: the one; characterized by the decomposition of CO_2 and evolution of oxygen; and another; comprising the photochemical reactions of the subsequent transformation of the primary assimilates; which is connected with their transfer and assimilation.

When carrying on the work described below; photosynthesis was understood by us in the strict meaning of the word; or as its first phase; according to Lubimenko;

we tried; moreover; to trace the way in which it was influenced by another process; *viz.* that of the growth of the plant.

As experimental material use was made of table and sugar-beet (*Beta vulgaris* subsp. *esculenta* and subsp. *altissima*). Both subspecies are most convenient for our purpose, being responsive to various stimuli and having been rather well investigated. The plants were grown on the beds of the Laboratory's experiment plot; by giving nitrogenic fertilizers and by watering them we were able to encourage the growth and the accumulation of substance by the plants; or to inhibit these processes by suspending the procedures.

Photosynthesis determinations were made according to Warburg (8) under constant external conditions: temperature, 25° C; CO_2 content; 0.206 per cent (to air volume); light; 11 000 luxes; saturation with water vapour; to utmost capacity, length of exposure, 30 minutes. Respiration was recorded at the same time. In the case of coinciding results the tests were run in threefold replication. Under experiment were always taken leaves that had been severed from the plant one hour prior to exposure and saturated with water to the utmost turgor, when wrapped in moistened blotting paper. An area 4 cm^2 large was cut out of the central portion of the leaf, care being taken to avoid any important veinlet. All the calculations have been made in mg of CO_2 per 1 dm^2 within 1 hour. The growth and weight of the experimental plants are characterized by Tables 1; 2 and 3.

Table 1

Beta vulgaris subsp. *esculenta*

Date	Regime	Leaf area of 1 plant in cm^2	Raw weight of one plant in g				Dry weight of one plant in g			
			Leaves	Cuttings	Roots	Total weight	Leaves	Cuttings	Roots	Total weight
28.VII	Nitrogen fertilizers .	1182	50.17	54.11	54.34	158.62	5.64	7.82	4.38	17.84
	Control	736	25.64	24.60	18.72	68.96	2.62	2.02	1.91	6.55
	Watering	1329	65.09	52.15	128.67	245.91	7.00	11.83	5.0	23.83
	Control	609	21.94	10,55	18.66	51.15	3.15	3.60	1.19	7.94

Table 2

Beta vulgaris subsp. *esculenta*

Date	Regime	Dry weight of one plant in g			
		Leaves	Cuttings	Roots	Total weight
8.VIII	Nitrogen fertilizers	89	109	105	304
	Control	47	62	45	154
	Watering	278	241	270	789
	Control	20	25	38	83

Table 3

Beta vulgaris subsp. *altissima*

Date	Regime	Dry weight of one plant in g			
		Leaves	Cuttings	Roots	Total weight
3.VIII	Watering	132	108	110	350
	Control	27	19	38	84
8.VIII	Watering	240	288	321	849
	Control	35	26	31	92

The course of growth is subject to rather essential variations according to the object experimented upon; the need of photosynthetic products seems also to differ sharply as to the case. Tables 4; 5 and 6 contain the figures of photosynthesis determined for different objects.

Table 4

Beta vulgaris subsp. *esculenta*

Date	Regime	mg CO_2 per hour dm^2	
		Photosynthesis	Respiration
28.VII	Nitrogen	8.14	1.53
	Control	2.09	1.98
	Watering	12.65	2.69
	Control	9.70	1.89

Table 5

Beta vulgaris subsp. *esculenta*

Date	Regime	mg CO_2 per hour dm^2	
		Photosynthesis	Respiration
8.VIII	Nitrogen	10.90	2.87
	Control	10.06	3.25
	Watering	12.40	3.77
	Control	10.06	3.25

Table 6

Beta vulgaris subsp. *altissima*

Date	Regime	mg of CO_2 per hour dm^2	
		Photosynthesis	Respiration
3.VIII	Watering	12.80	2.03
	Control	10.40	1.73
8.VIII	Watering	11.00	1.80
	Control	11.00	2.60

As may be inferred from the figures, there is no relation between growth; accumulation of matter and photosynthesis. In both subspecies of beet the primary stage of photosynthesis passes independently; without any functional correlation with growth; matter accumulation and decomposition of CO_2. The rate of CO_2 decomposition per unit area is about the same in such plants as differ sharply by the development of their organs and by the rate of growth.

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PHYSIOLOGY

VOCAL IMITATION IN THE *PASSERIFORMES* AS ONE OF THE SPECIFIC FEATURES OF THEIR HIGHER NERVOUS ACTIVITY

By A. N. PROMPTOV

(Communicated by L. A. Orbeli, Member of the Academy, 29.III.1944)

1. Among all other vertebrates the birds are endowed with the most perfect vocal instrument; the syrinx. The function of this organ; combined with that of other organs (trachea; glottis; air-sacs, *etc*). enables them to utter a great variety of sounds, and to modify the timbre and pitch of the latter. Especially accomplished in this respect are the *Passeriformes* songsters (*Passeres oscines*). Special morphological studies started as far back as more than 300 years ago ([1], [6], [8], [27], [10]) and supplemented whithin the recent years by thoroughgoing investigations have fully elucidated the acoustical aspect of the phenomenon. They failed, however, to inquire to any depth into the knowledge of its physiological and biological mechanism ([11], [12], [30]). The structure of the syrinx has been found to display a striking likeness not only in closely related species of sing-birds; but among the order as a whole, as well. And yet every species is known to have their own song, which is an as typical specific feature as the colouring of the plumage, the size and other morphological characters ([22]). Hence it follows that the specific peculiarities of the song are not due to the anatomical differences in the structure of the syrinx but their causes are of purely physiological nature and consist in a definite stereotypic complex of muscular movements, in which the entire vocal apparatus is involved.

To use a picturesque language; a melody owes its tune to the combination and succession of the sounds which the performer makes his instrument to produce, rather than to the instrument itself.

The complex of reactions (contractions) of the muscles of the syrinx, trachea and other organs with which they are functionally connected; continuously reccurring and attaining in the songs of many species (say, the thrushes, warblers) a very high degree of complexity, is connected with definite centres of the brain and with nervous transmission ways (chiefly with *n. hypoglossus*) ([11], [12]). In its essence it is a reflex process of highest complexity. But this is merely the one aspect of the phenomenon.

On the basis of a most subtle operation of the acoustic analyser; a young bird which learns to sing imitates the tunes of other individuals of its species or any other sounds in the surrounding medium, and compiles a typical song of its own.

In this process; aside from a definite hereditary basis; a very important place belongs to the biocoenosis ([9]) and to the mode of life of each separate species, which are responsible for the manysided biological rôle of the voice and song of the birds ([2], [3], [5], [12], [15], [17], [18]).

2. Direct observations carried out on singing birds furnish us such data as point to a striking ability of certain species to reproduce in a most exact manner a vari-

ety of sounds ([9], [16], [4]). The song of some of these species (among our ornithofauna especially of various warblers and shrikes) consists almost entirely of imitated sounds.

They reproduce not only voices of other birds; their neighbours; but those of most diverse animals they use to hear under natural conditions (for example, frogs).

But in species whose songs do not comprise many sounds imitated from other species; the working out of a normally specific cadence proceeds largely by way of imitating old songsters.

To make a more detailed analysis of the imitation ability of various *Passeriformes*, it is necessary closely to observe young birds to work out their song under artificial conditions.

With this aim in view we have reared at the laboratory young birds taken from the nest at as early an age as possible (some of them had been taken when still blind). Within the last six years of our work, carried on jointly with E. V. Lukina; more than 100 young birds belonging to the most various families of *Passeres* ([24]) have been brought up. As a rule, the young birds were prevented from hearing the song of adult individuals of the same species; they were allowed, however, to listen to various sounds, and to the songs of birds of other species kept in the same room.

Some hybrids have also been bred which gave us definite data, shedding light upon the hereditary basis of the development of singing. The conclusions we have arrived at on the basis of personal observations and experiments go largely to confirm the data available in literature ([4], [7], [13], [14], [29]). They can briefly be summarized in the following way.

3. The c a l l s in birds are of hereditary nature; they are reflex expressions of various emotional conditions (fright, alarm, hunger, *etc.*), and of kinaesthetic correlations, as well.

In an overwhelming majority of bird species the hereditary basis of s o n g i s manifest in the following general features only: 1) general ability to reproduce sounds (complicate or poor combinations of sounds); 2) general specific character of the song (a long or a short song, comprising reiterations, or without them, *etc.*); 3) the tempo of performance (lively, moderately or leisurely). These hereditary elements of the structure of a song are fundamental characters, probably depending on definite structural peculiarities of the brain centres and of the transferring ways, as well as on the type of the nervous system (this refers especially to the tempo of the song).

In order to investigate the hereditary basis in the formation of the song and in the development of the imitating ability, use was made of hybridization of closely related species and genera. From the material available at the time being, which consists of hybrids between some finches (goldfinch, siskin, canary), one can conclude that there exist certain inherent specific «inclinations» in the formation of the song, even if it is combined of borrowed sounds only. Thus, for example, the hybrids of the siskin and the canary have been found to be able to work out loud canary trills without any teacher; at the same time they have inherited from their father, a siskin, the capacity of imitating the song of various other wild birds in a most clever way. The song of the hybrids between the goldfinch and the canary, which have never heared to sing a canary-male, had sometimes timbres peculiar to the latter.

In a long pedigree of hybrids of siskin and canary, comprising several generations ([20], [21]), individual distinctions have been recorded in the structure of the song in hybrids of different generations. Unfortunately, the rather ample hybridization scope among *Passeres* is nevertheless confined almost exclusively to crosses between families. Wider diversities in the vocal peculiarities between more remote groups of *Passeres* remain out of the limits of hybridization, so that this method cannot receive a wide application.

In some bird species the timbre of voice is inherited (this is most conspicuous in *Hypolais icterina*). But there are also many species endowed with good imitation capacities, which are lacking any specific inherent timbre. Very few species are

able to work out their song without any «teacher»; and those which do so have but a very primitive assortment of tones (for example, *Phylloscopus sibilatrix*; *Ph. collybita*, *Emberiza citrinella*, *Anthus trivialis*, *Chloris chloris*). Most of the species are unable to work out their normal specific type of song without having listened to old songsters. Young birds separated from their parents or without any influence of other adult individuals of the same species, have been found to develop quite an aberrant song which often differed markedly from the specific one.

4. In order that young birds normally develop their song under natural conditions, it is important that they hear their father sing at a very early age, best of all during the very first days upon hatching in their nest [29].

The early attempts of young males to utter a song are nothing else than an involuntary desire to reproduce sounds and to exercise their vocal muscles; both are probably stimulated by sex hormones [19, 24, 31]. It is noteworthy that these early attempts are much alike in the most various species. They represent a quite undefinable warbling and twittering which may continue for a rather long time. In a few species only an attentive ear is able to discern certain peculiarities of the timbre (wheatears, redstarts, finches, pipits). This most interesting fact, *viz.* the similarity in the song of various bird species at an early stage of development, goes once more to confirm that in the case of an identical anatomical structure of the syrinx scarcely any specific distinctions may be detected in such an early «chatter» of young birds. Such distinctions become manifest only after a definite stereotype of muscular movements of the syrinx and of other organs has been worked out as a result of numerous repetitions. The young songster soon includes in its twitter all the sounds that happen to be uttered around in stereotypic combinations, as well as the voices of other birds. Out of them the young songster makes a peculiar but quite individual tune. In the case a definite stereotype of sounds is missing in the surrounding medium, the young bird may conserve its juvenile twitter for a very long period of time (up to three years in our experiments). It is of interest to point out that young beginners hearing around them many different species to sing at once, «recognize» in some way the song of their own species and imitate it more readily and in a more perfect manner than the song of other species [15, 16]. Moreover, if a young bird brought up without parents and outside the nest has already developed a definite though quite peculiar song without any teacher, it abandons it as soon as it happens to hear a typical specific song, which it tunes up almost at once.

All these data point to the important part played by the imitation ability in the development of a normal specific song almost in all sing-birds.

5. The high ability of exact vocal imitation has been developed in the sing-birds in the course of evolution as a result of a long natural selection [2, 18, 32]; the rôle it plays in the biology of modern birds is very important. The nervous activity of birds, especially at the period of reproduction, is intimately connected with a highly exact work of the auditory and optical analysers. Each change in the physiological state of the bird, almost every movement, is accompanied with a definite type of cries, calls or song [22, 25]. In spring the song of the males, typical for each species, serves for the females as an «recognition signal», and curious enough, such species as are the most alike as to the coloration of the plumage and general habitus, differ sharply as to their songs (for example, among the wrens, warblers) [17]. A male whose voice is not loud enough has less chances to preserve its nesting place. Those birds which are mocking by their song the voice of their neighbour species seem to be in an especially favourable position, since their «territory signal» extends outside the limits of the species, and probably secures for them better nesting conditions [8].

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EXPERIMENTAL MORPHOLOGY

STUDIES IN REPEATED REGENERATION

By W. N. DOBROKHOTOV and G. I. GINZBURG

(Communicated by I. I. Schmalhausen, Member of the Academy, 3.V. 1944)

Two essentially different standpoints are known to exist in the approach to the problem of the origin of regeneration material. According to one of them, the development of a regenerate proceeds at the expense of the differentiating tissues of a remain of an organ, after the elements of these tissues undergo dedifferentiation. According to the other viewpoint, the regenerate is supposed to develop from indifferent pluripotent cells. It is the latter interpretation which prevails when regeneration in invertebrates is considered. In their attempts to solve this problem some authors had recourse to the study of repeated regenerations.

Working with amphibians, Blacher (1) has shown that repeated amputations do not reduce the size of the regenerates, and that the intensity of secondary regenerations considerably exceeds that of the primary one. This fact made him question the idea of indifferent cells being responsible for regenerations.

According to observations made by Chranowa (2), the period of time necessary for the repeated regenerations of the cephalic or caudal parts of planarians is found gradually to decrease at the beginning of the experiment, and it is not until a considerable number of operations have been made that regeneration takes place after a longer period, and finally fails altogether. In his experiments with repeated regeneration of the pedicel part of hydrae, Goetsch (3) succeeded in inhibiting their budding. In so far as it is the interstitial elements he believes to be responsible for the development of the bud and of the regenerate; he accordingly associates the inhibition of budding observed in his experiments with an influx of these elements to the place of the formation of the regenerate.

It should be pointed out that the lack of histological control in any of the experiments referred to above makes the conclusions arrived at anything but convincing.

Very interesting are the observations made by Kanajew (5) with repeated regeneration of the cephalic part of starving hydrae. Most of the latter perished without having passed the second regeneration, only a few animals have been found to form small tentacles. Such hydrae possessed but a small number of interstitial cells as compared to normal individuals. The author supposes this decrease in the number of interstitial cells to be due to their being used up for the regeneration of tentacles or, more strictly speaking, for the restitution of stinging cells, cnidae, which accounts for the suppressed secondary development of tentacles.

The purpose of the present work has been to check up the possibility of repeated regenerations in hydrae subjected to starvation. In the subsequent there was planned a detailed histological investigation of repeatedly regenerating individuals, made in order to find out the relation between interstitial elements and regeneration. If the latter is really brought about by the interstitial elements, then in the case of repeated regeneration their number should gradually decrease in those regions which adjoin to the place of amputation, or else throughout the organism, if we take for granted the migration of interstitial cells (4). If repeated regeneration were not accompanied by a reduction in the store of interstitial cells and if the lat-

ter did not proliferate, this should be taken to mean that they are not involved in regeneration.

For your experiments we made use of hydrae (*Pelmatohydra oligactis*) obtained some 1—2 days prior to the experiments from under natural conditions.

Set A (30.VI—15.VII). During the first amputation and those which followed, up to $^1/_2$ of the stomachal part was removed; neither in this experimental set nor in the subsequent ones did we proceed to the next operation until a new hypostomal cone was formed and the regenerating tentacles attained about a third or a half of their original length.

The experiment comprised 24 hydrae. 7 of the animals of this set perished without having passed the first regeneration, 4—upon the first regeneration. For histological examination have been fixed 2 hydrae after the first regeneration, 4 after the second and the third one, and 3, after the fourth regeneration.

In order to make clear the influence of starvation, a control set was kept, consisting of 10 animals which have not been operated and have been fixed before the end of the experiment.

Set B (6.VII—17.VII) differed from the preceding one in that the amputations were made closer to the zone of tentacles, so that about $^1/_5$ of the stomachal part of the animal was removed. The set consisted of 30 experimental and 12 control animals. 6 of them perished after the third regeneration, and 1, after the fourth one. One animal has been fixed after the second regeneration; 8, upon the third one; 10, upon the fourth, and 2, upon the fifth regeneration. Two hydrae have incidentally perished at the beginning of the experiment.

Set C (23.VII—3.VIII). Amputation was practised at the same level as in the preceding set. The aim of this set was to secure sufficient material for the histological examination of such animals as have passed a second or a third regeneration. The set consisted of 37 experimental and 5 control animals. 2 of them perished without having passed a single regeneration; 3 upon the first one, and 1, upon the second regeneration. The rest of hydrae were fixed after the second or the third regeneration.

Set D (20.VII—7.VIII). Amputation made at the same level as in set B. The purpose of this set was to reveal the maximum of repeated regenerations possible. The experiment comprised 20 hydrae. 2 animals perished upon the third and second regeneration; 3, after the fourth; 5, after the fifth; 3, after the sixth; and 4, after the seventh regeneration. One of the hydrae has formed two buds at the very beginning of the experiment and was excluded from the set.

In all the experimental sets the regenerating animals decreased in size after each new amputation. Thus, after the 5th amputation nothing else has been left of a regenerating hydra than a small portion of the stomachal part and a pedicel.

The results of preceding sets make it evident that repeated regeneration of the hypostomal part and of the tentacles may take place under conditions of starvation. The first regenerations (from one to four in number) seem to proceed without any difficulties in most of the animals. The high rate of mortality recorded among the hydrae of set A upon the first amputation was due to their infection with kerona.

Set \ Date of amputation	I—II	II—III	III—IV	IV—V	V—VI	VI—VII	VII—VIII
A	52	76	98	88	—	—	—
B	68	55	51	44	45	—	—
C	44	42	60	56	66	62	84
D	54	47	48	—	—	—	—
Mean . .	54.5	55.0	64.0	63.0	55.0	62.0	84.0

Repeated amputations being always practised at the same stage of regeneration, it has been found possible to calculate at what intervals the amputations should be made, in order that regeneration might take place after them.

In the table are given the mean intervals (in hours) between the amputations within each set.

Within each set the intervals between the amputations made to individual hydrae varied but very little. Only in a few separate cases there were rather considerable deviations, but these cases have been omitted when calculating the mean values of the intervals. Thus, in set A the interval between the II and the III amputation in one specimen was equal to 168 hours, in another one, the interval between the III and the IV amputation was equal to 192 hours. In set C the interval between the V and the VI amputation was equal to 168 hours, while in set D the interval between the I and the II amputation in one individual case lasted 144 hours, and in another, 120 hours (between the III and the IV amputation this time). In such cases the animals were mostly soon subject to decay without undergoing any regeneration.

It can easily by seen from an analysis of the table that there is no important increase in the intervals between the subsequent regenerations. This is especially well illustrated by the mean figures given at the bottom of the table. Sets A and C showed some deviations from the general rule, however. The results of set A might possibly have been affected by the fact that the experiment was infected with kerona and by a sharp drop in temperature which took place between the 3rd and the 6th of July. In set D there was no increase in the periods of regeneration, except for the last amputations. This phenomenon should possibly be referred to the lengthy starvation and general emaciation of the animals, due to the long period of time during which the experiment was carried out (15—17 days). The degree of restoration of the part severed may be estimated after the number of tentacles regenerated. The calculation of the average number of tentacles after each regeneration gave the following figures for all the experimental sets; the original number of tentacles being 5.4:

Regeneration	I	II	III	IV	V	VI	VII
Number of regenerating tentacles .	3.3	3.1	2.4	1.8	1.8	1.7	1.3

The table shows the number of tentacles gradually to decrease from one regeneration to the subsequent one. Whether this is actually due to a loss of interstitial elements which are necessary for the regeneration of tentacles, as believed by Kanajew, or to a prolonged starvation and exhastion of the organism, cannot be decided unless the material prepared is subjected to histological analysis. The results of the latter will be reported in our next communication.

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